Supporting Information

The Golden Goal of Entatic State Model Design: Lowering the Internal Reorganization Energy Leads to Exponential Increase in Electron Transfer Rate

Tobias Seitz, Aylin Karabulut, Rafael Mugi Suzuki, Alexander Hoffmann, Joshua Heck, Sonja Herres-Pawlis*

Table of Contents

1. Experimental Part

1.1 Data Availability

The obtained analytical stopped-flow-UV/Vis spectroscopic data and cyclic voltammetry data, as well as the optimized coordinates from DFT computations are provided in the RADAR4Chem repository.

DOI:10.22000/ab0bmuwhdgfs0tqq

Experimental data like NMR-, mass- and IR-spectra can be viewed in the Chemotion repository.

https://dx.doi.org/10.14272/collection/ToS_2024-11-28

1.2 General Aspects, Chemicals and Solvents

All reactions and manipulations that require inert conditions were carried out under nitrogen atmosphere (99.996 %), with the nitrogen gas being dried by passage through a column filled with SICAPENT®. If necessary, the solvents were dried by standard literature procedures and degassed by three circles of freeze pump thaw.[2] The Vilsmeier salt chloro-*N*,*N*,*N*',*N*'-tetramethylformamidinium chloride (TMG-VS) was synthesized according to the literature.[3] All other chemicals were purchased from commercial suppliers and used without further purification.

1.3 Analytics and Compound Purification

1.3.1 Nuclear Magnetic Resonance Spectroscopy

The nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance III HD 400 or a Bruker Avance II 400 nuclear resonance spectrometer at 25 °C. The ^{1}H NMR spectra were referenced to the solvent residual signal and the ^{13}C{H} NMR spectra were referenced to the solvent signal. The solvent signals in the ^{1}H and ^{13}C{H} NMR spectra were defined relative to the external standard tetramethylsilane (TMS) as reported in the literature.[4] The chemical shifts of the compounds were assigned with the use of two-dimensional NMR spectroscopic experiments (COSY, HSQC, HMBC, APT). For the Bruker Avance III HD 400, the software Topspin (Version 3.5 pl

7) from Bruker Corporation and for the Bruker Avance II 400, the software TopSpin (Version 2.1) from Bruker Corporation were used for data acquisition. For visualization and examination of the NMR spectra the software MestReNova (Version 12.0.1-20560) from Mestrelab Research was used. Selected NMR spectroscopic data were deposited as original data in the Chemotion Repository and are published under an Open Access model.[5] The link to the original data is given in the analytical description.

1.3.2 Electron Spray Ionization High Resolution Mass Spectrometry

The electron spray ionization (ESI) high-resolution (HR) mass spectra were performed and recorded on an UHR-TOF Bruker Daltonik maXis II or a ThermoFisher Scientific LTQ Orbitrap XL. Detection was either in positive or in the negative ion mode. The mass spectrometer was calibrated subsequently to every experiment via direct infusion of a L-proline sodium salt solution, which provided a *m*/*z* range of singly charged peaks up to 3000 Da in both ion modes. For the ThermoFisher Scientific LTQ Orbitrap XL the source voltage was 4.49 kV and the capillary temperature was 299.54 °C. The tube lens voltage was set between 110 and 130 V. For the Bruker Daltonik maXis II, the software otofControl (Version 6.3, Build 0.5) and Compass DataAnalysis (Version 5.3, Build 556.396.6383) from Bruker Corporation and for the ThermoFisher Scientific LTQ Orbitrap XL, the software Thermo Xcalibur (Version 4.5.445.18) were used for data acquisition and examination. Selected ESI-HRMS data were deposited as original data in the Chemotion Repository and are published under an Open Access model.[5] The link to the original data is given in the analytical description.

1.3.3 Fourier Transform Infrared Spectroscopy

The Fourier transform infrared (FTIR) spectra were recorded on a Shimadzu IRTracer 100 using a CsI beam splitter in combination with an attenuated total reflectance (ATR) unit (Quest model from Specac utilising a robust monolithic crystalline diamond) in a resolution of 2 cm^{-1}. For data acquisition, the software LabSolution IR (Version 2.15) from Shimadzu Corporation was used. Selected FTIR spectroscopic data were deposited as original data in the Chemotion Repository and are published under an Open Access model.[5] The link to the original data is given in the analytical description.

1.3.4 Thin Layer Chromatography

Thin layer chromatography (TLC) was performed with TLC sheets from MACHEREY-NAGEL pre-coated with a layer of silica gel 60 with a thickness of 0.20 mm and a fluorescent indicator.

1.3.5 Column Chromatography

Column chromatography was performed with Geduran® Si 60 (40-63 µm) from Merck or with MP Alumina B - Super I from MP Biomedicals.

1.3.6 Single-Crystal X-Ray Diffraction

The ellipsoid plots and crystallographic data of **C1-PF_6** to **C4-OTf** are presented in Fig. S1 to S4 and in Table S2 and S3. The data were collected with a four-circle goniometer Stoe Stadivari with Dectris Pilatus3 R 200 K hybrid pixel detector using GeniX 3D high flux Mo-K_α radiation (λ = 0.71073 Å) at 150 K for **C1-PF_6** and at 100 K for every other compound. The temperature was controlled by an Oxford Cryostream 800. Crystals were mounted on cryoloops with perfluorinated oil. Data were collected with X-Area Pilatus,[6] indexed with X-Area Recipe[7] and integrated with X-Area Integrate.[8] A spherical absorption correction was performed with STOE X-Red32 followed by a multi-scan absorption correction and scaling of reflections with X-Area LANA.[9]

The structures were solved by intrinsic phasing (ShelXT[10]) or direct methods (ShelXS[11]) and refined against F^2 with the full-matrix least-square method of ShelXL[12] using the graphical user interface ShelXle.[13] Non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were localized at idealized positions and refined with isotropic displacement parameters. All methyl groups were allowed to rotate but not to tip.

In **C2-OTf** it was not possible to model the disordered solvent molecules (H_2O) in an adequate manner, and the data set was treated with the SQUEEZE routine as implemented in PLATON.[14] **C3-PF_6** is a twin and the data set was treated with the TwinRotMat routine as implemented in platon (rotation axis in reciprocal space (2 -1 0), twin law 1 0 0 -1 -1 0 0 0 -1).[14]

Full crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary no. CCDC – 2401616 for **C1-PF_6**, CCDC – 2401617 for **C2-OTf**, CCDC – 2401618 for **C3-PF_6** and CCDC – 2401619 for **C4-OTf**. Copies of the data can be obtained free of charge on

application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

1.3.7 Powder Diffraction

PXRD experiments were performed at ambient conditions on flat samples using a STOE STADI P diffractometer with Debye-Scherrer geometry (Cu-Kα1, λ = 1.540598 Å, STOE image plate detector IP-PSD).

1.3.8 Cyclic Voltammetry

The measurements were performed with a METROHM AUTOLAB PGSTAT 101 potentiostat using a three-electrode arrangement with a Pt disc working electrode (1 mm diameter), a Pt wire as counter electrode and an Ag/AgCl (in saturated ethanolic LiCl) reference electrode. The measurements were performed in MeCN and 100 mmol/L NBu_4PF_6 with a sample concentration of 1 mmol/L at room temperature. Ferrocene was added as an internal standard after the measurements of the sample and all potentials are referenced relative to the Fc/Fc^+ potential. Cyclic voltammograms were measured with 200 mV s^{-1}, 100 mV s^{-1}, 50 mV s^{-1} and 20 mV s^{-1}. For data acquisition and examination, the software NOVA 2.1.5 (Build 7691) from Metrohm Autolab was used. For visualization of the cyclic voltammograms the software OriginPro 2021b (Version 9.8.5.212) from OriginLab was used. The cyclic voltammograms are depicted in Fig. S10 to S12, more detailed data can be viewed in table S5.

1.3.9 Electron Paramagnetic Resonance Spectroscopy (EPR)

The electron paramagnetic resonance (EPR) spectroscopic measurements were performed with a Magnettech Miniscope MS 400. The setup included the Resonator Rectangular TE102 and a microwave frequency counter Magnettech FC. The solutions of the Cu(II) complexes were prepared as a 5 mM solution in MeCN. The measurements were performed in EPR tubes, closed with Critoseal® wax, at 77 K. The experiments were carried out using a microwave frequency of 9.428 ± 0.001 GHz, a B_0 field of 328 mT, a B_0 sweep of 180 mT and a modulation amplitude of 0.40 mT. For data acquisition, the software MiniscopeCtrl (Version 1.0.0.1542) from Magnettech GmbH was used. The spectra were simulated with the Matlab tool EasySpin 6.0.0 to obtain further information about the spin system.[15] The applied simulation function was “pepper”, a function

for solid state continuous wave EPR with an arbitrary number of spins. For visualization of the EPR spectra, the software OriginPro 2021b (Version 9.8.5.212) from OriginLab was used. The spectra can be seen in Figures S17 to S21, the g- and A-values, as well as theoretical and experimental τ_4-parameters of the Cu(II)-compounds are provided in Table S7. While not pronounced, a more flattened structure (smaller τ_4-value) yields smaller values for $g_{\parallel}$, linking the structures' flattening to the shape of the EPR spectra.

1.3.10 UV/Vis Spectroscopy

The UV/Vis spectra were recorded with a Cary 60 spectrophotometer from Agilent Technologies in combination with quartz glass cuvettes (1 mm, QS) at room temperature. The solutions (c = 1 mM) were prepared from the corresponding complexes. For data acquisition, the software Cary WinUV (Version 5.1.3.1042) from Agilent Technologies was used. For visualization of the UV/Vis spectra, the software OriginPro 2021b (Version 9.8.5.212) from OriginLab was used. The spectra are depicted in Fig. S7 and Fig. S8. An overlay of the Cu(II) UV/Vis spectra of the herein reported systems and the other discussed 2-substituted TMGqu-systems is provided in Figure S9. No strong correlation between the structure of the Cu(II)-complexes and their spectra can be seen, likely because the NMe_2- and Ph-substituents do affect the optical properties of the complexes.

1.3.11 Stopped-Flow UV/Vis Spectroscopy

The stopped-flow UV/Vis spectroscopic measurements were performed with a HI-TECH Scientific SF-61SX2 device with a diode array detector. The optical light path for transmission of the quartz glass cuvette was 10 mm. The mixing time is given by HI-TECH to amount to 2 ms. UV/Vis spectra in a wavelength range of 300 nm to 800 nm were detected with temporal resolutions of 0.75 to 7.5 s. The analyses were carried out with the TgK Scientific program Kinetic Studio 4.0.8.18533. UV/Vis spectra (300–800 nm) were detected. For visualization and examination of the results the software OriginPro 2021b (Version 9.8.5.212) from OriginLab was used.

The cross reactions starting from $[Cu(TMG2Phqu)_2]PF_6{\cdot}CH_2Cl_2$ (**C1-PF$_6$**) and $[Cu(TMG2NMe_2qu)_2]PF_6{\cdot}2\ CH_2Cl_2$ (**C3-PF$_6$**) were conducted using the counter complex $[Co(bpy)_3](PF_6)_3$. The cross reactions starting from $[Cu(TMG2Phqu)_2](OTf)_2{\cdot}0.5\ H_2O$ (**C2-OTf**) were

conducted using the counter complex **C3-PF_6**. To measure the kinetics of the cross-reaction, a solution of the measured complex (0.2 mM) in MeCN was mixed with up to five differently concentrated solutions (with reactant in excess) of employed counter complex and the increase of the solutions' absorptions at a constant wavelength were observed. Every measurement was performed twice. Employed concentrations are listed in Table S1.

Due to the differently concentrated solutions of the counter complexes, the ionic strength was not the same for all analyzed cross reactions and varied for every solution of the counter complex with a specific concentration. The ionic strength influences the activity coefficients of the reactants. However, the influence on the activity coefficient is not significant for the determination of k_{12}. Therefore, for simplification of the concentrations the activity coefficients were not considered for the determination of k_{12}. The resulting plots are depicted in Fig. S12 to S14.

Table S1: Employed counter complex-concentrations for each reported stopped-flow UV/Vis spectroscopic measurement.

Measured Complex	$[Cu(TMG2Phqu)_2]PF_6\cdot CH_2Cl_2$ (**C1-PF_6**)	$[Cu(TMG2NMe_2qu)_2]PF_6\cdot 2\,CH_2Cl_2$ (**C3-PF_6**)	$[Cu(TMG2Phqu)_2](OTf)_2\cdot 0.5\,H_2O$ (**C2-OTf**)*
Counter Complex	$[Co(bpy)_3](PF_6)_3$	$[Co(bpy)_3](PF_6)_3$	**C3-PF_6**
c_1 [mmol/L]	1.0	1.0	1.0
c_2 [mmol/L]	1.5	1.5	1.67
c_3 [mmol/L]	2.0	2.0	2.34
c_4 [mmol/L]	2.5	2.5	3.0
c_5 [mmol/L]	3.0	3.0	-

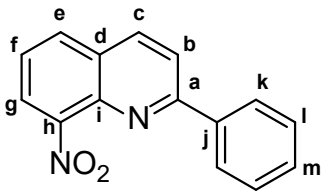
*__C2-OTf__ was measured against 4 concentrations to conserve the amount of available **C3-PF_6**.

2 Synthesis

2.1 Synthesis of TMG2Phqu (L) and corresponding precursors

2.1.1 Synthesis of 8-nitro-2-phenylquinoline

The procedure was inspired by Ortíz-Alvarado, Chacón-García and Solorio-Alvarado *et al.*[16]



250.26 g/mol

A Schlenk-flask was evacuated and flushed with nitrogen gas three times. Under nitrogen counterflow, it was charged with 2-chloro-8-nitroquinoline (2.00 g, 9.59 mmol, 1.00 equiv.), phenylboronic acid (1.40 g, 11.5 mmol, 1.20 equiv.) and palladium triphenylphosphane (295 mg, 255 µmol, 0.0266 equiv.). The flask was again evacuated and flushed with nitrogen three times, then toluene (20.0 mL) and water (4.00 mL) were added under nitrogen counterflow. The flask was connected to a reflux condenser under inert conditions and left stirring at 110 °C for 18 h. Afterwards, the reaction mixture was allowed to cool to room temperature and the mixture was extracted with DCM (3x 20 mL). The combined organic phases were dried over $MgSO_4$, and the remaining solvent was removed under reduced pressure. The resulting red oil was purified using column chromatography (pentane/ethyl acetate = 3/2, R_f = 0.46), the solvent was removed under reduced pressure and the product was dried *in-vacuo*. 8-nitro-2-phenylquinoline (1.52 g, 6.07 mmol, 63% yield) was obtained as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm] = 8.29 (d, *J* = 8.8 Hz, 1H, H-c), 8.24 – 8.18 (m, 2H, H-k), 8.05 – 7.97 (m, 3H, H-b, H-e, H-g), 7.58 – 7.49 (m, 4H, H-f, H-l, H-m).

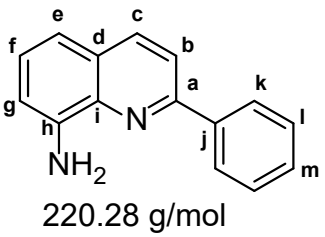
^{13}C NMR (101 MHz, $CDCl_3$) δ [ppm] = 159.0 (C-a), 148.8 (C-h), 139.6 (C-i), 138.5 (C-j), 137.2 (C-c), 131.9 (C-e/C-g), 130.7 (C-m), 129.3 (C-l), 128.4 (C-d), 128.0 (C-k), 125.2 (C-f), 124.0 (C-e/C-g), 120.5 (C-b).

HR-ESI-MS: $[M+H]^+$ (m/z (%) $[M+H]^+$, M+H = $C_{15}H_{11}N_2O_2$) found: 251.08116 (100), 252.08442 (17), 253.08664 (2). Calculated: 251.08150 (100), 252.08486 (16), 253.08821 (1).

IR (ATR, ṽ) = 3094 (vw), 3055 (vw), 2955 (vw), 2920 (vw), 2870 (vw), 2855 (vw), 1622 (w), 1612 (vw), 1599 (m), 1582 (w), 1564 (vw), 1553 (w), 1520 (vs), 1506 (vs), 1489 (s), 1458 (w), 1443 (m), 1423 (w), 1377 (w), 1354 (vs), 1323 (s), 1310 (w), 1287 (m), 1223 (w), 1215 (w), 1207 (w), 1182

(w), 1157 (w), 1146 (w), 1103 (vw), 1074 (w), 1049 (vw), 1022 (w), 1001 (vw), 993 (vw), 980 (w), 924 (w), 881 (m), 858 (w), 845 (vs), 818 (vw), 795 (s), 760 (vs), 731 (w), 702 (m), 691 (vs), 658 (vs), 619 (vw), 604 (w), 565 (vw), 550 (w), 513 (w), 501 (w), 457 (vw), 442 (vw), 432 (w) cm^{-1}.

2.1.2 Synthesis of 2-phenylquinolin-8-amine



220.28 g/mol

A Schlenk-flask was evacuated and flushed with nitrogen three times. 8-nitro-2-phenylquinoline (2.69 g, 10.7 mmol, 1.00 equiv.) and palladium on charcoal (60.0 mg, 10 wt-% Pd, 56 µmol, 0.00525 equiv. Pd) were added under nitrogen counterflow; the flask was subsequently evacuated and flushed with nitrogen three times. The powder in the flask was allowed to settle before methanol (120 mL) was slowly added under nitrogen counter flow. The pressure inside was reduced until the solvent started to boil and then flushed with nitrogen. Then, the nitrogen atmosphere was substituted with hydrogen gas using balloons. Afterwards, the reaction was stirred at room temperature for 4 hours with the hydrogen balloons attached. The solvent was removed under reduced pressure, the crude product was dissolved in ethyl acetate (100 mL) and filtered through silica to remove the catalyst, the solvent was subsequently removed under reduced pressure. The resulting red solid was further purified using column chromatography (hexane/ethyl acetate = 3/1, R_F = 0.35), after which the solvent was removed under reduced pressure and the product was dried *in-vacuo*. 2-phenylquinolin-8-amine (1.88 g, 8.54 mmol, 79% yield) was obtained as a yellow solid and stored under inert conditions to avoid decomposition.

^{1}H NMR (400 MHz, CD_2Cl_2) δ [ppm] = 8.22 (dd, *J* = 8.4, 1.3 Hz, 2H, H-k), 8.16 (d, *J* = 8.6 Hz, 1H, H-c), 7.90 (d, *J* = 8.6 Hz, 1H, H-b), 7.58 – 7.51 (m, 2H, H-l), 7.50 – 7.44 (m, 1H, H-m), 7.33 (t, *J* = 7.9 Hz, 1H, H-f), 7.17 (dd, *J* = 8.1, 1.3 Hz, 1H, H-g), 6.95 (dd, *J* = 7.5, 1.3 Hz, 1H, H-e), 5.14 (s, 2H, H-N).

^{13}C NMR (101 MHz, CD_2Cl_2) δ [ppm] = 154.3 (C-a), 144.8 (C-h), 139.9 (C-j), 138.3 (C-i), 137.2 (C-c), 129.5 (C-m), 129.1 (C-l), 128.2 (C-d), 127.7 (C-f), 127.6 (C-k), 119.2 (C-b), 115.8 (C-g), 110.3 (C-e).

HR-ESI-MS: $[M+H]^+$ (m/z (%) $[M+H]^+$, M+H = $C_{15}H_{13}N_2$) found: 221.10713 (100), 222.11041 (17), 223.11365 (1). Calculated: 221.10733 (100), 222.11068 (16), 223.11404 (1).

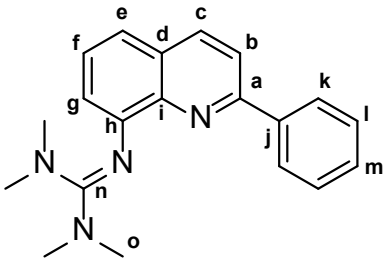
$[M+Na]^+$ (m/z (%) $[M+Na]^+$, M+Na = $NaC_{15}H_{12}N_2$) found: 243.08912 (100), 244.09238 (16), 245.11479 (6). Calculated: 243.08927 (100), 244.09262 (16), 245.08966 (1).

$[M+K]^+$ (m/z (%) $[M+K]^+$, M+K = $KC_{15}H_{12}N_2$) found: 259.06310 (100), 260.06633 (17), 261.06195 (7). Calculated: 259.06321 (100), 260.06656 (16), 261.06133 (7), 261.06992 (1).

IR (ATR, ṽ) = 3431 (w), 3310 (w), 3051 (w), 3036 (w), 1614 (m), 1589 (s), 1578 (m), 1560 (w), 1553 (w), 1508 (s), 1491 (vs), 1470 (vs), 1443 (w), 1429 (s), 1375 (vs), 1342 (s), 1337 (s), 1302 (w), 1298 (w), 1285 (m), 1273 (m), 1227 (w), 1155 (vw), 1128 (m), 1103 (w), 1086 (w), 1076 (w), 1055 (vw), 1020 (w), 999 (vw), 972 (vw), 966 (w), 959 (vw), 918 (vw), 891 (vw), 881 (w), 843 (w), 831 (vs), 810 (vw), 760 (vs), 750 (vs), 723 (w), 689 (vs), 644 (w), 588 (w), 569 (w), 550 (w), 534 (w), 525 (w), 501 (w), 484 (w), 463 (w), 422 (vw) cm^{-1}.

2.1.3 Synthesis of TMG2Phqu (L)

The guanidine synthesis was performed following a slightly modified procedure of Herres-Pawlis *et al.* which itself is based on the procedure of Kantlehner et al.[3b, 17]



318.42 g/mol

A preheated Schlenk-flask was charged with 2-phenylquinolin-8-amine (700 mg, 3.18 mmol, 1.00 equiv.) and TMG-VS (650 mg, 3.80 mmol, 1.20 equiv.) and acetonitrile (abs., 30.0 mL) under nitrogen counterflow. Triethylamine (639 mg, 880 µL, 6.31 mmol, 1.99 equiv.) was added under nitrogen counterflow and the reaction mixture was heated to reflux for 90 minutes under stirring and subsequently allowed to cool to room temperature. An aqueous KOH solution (25 mL, 50 wt-%) was added to the reaction mixture and the aqueous phase was extracted with acetonitrile (3x 50 mL). The organic layer was separated, dried over Na_2SO_4 and the remaining solvent was removed under reduced pressure. The resulting brown oil was then dissolved in small amounts of DCM and filtered over alumina with DCM as eluent, after which the solvent was removed under reduced pressure. The resulting yellow oil was then heated under vacuum ($<10^{-1}$ mbar), starting at 100 °C and rising to 250 °C, to remove any remaining urea derivative. TMG2Phqu (710 mg, 2.23 mmol, 70% yield) was obtained as a yellow, wax-like solid. The product needs to be stored under inert conditions to avoid protonation.

^{1}H NMR (400 MHz, CD_2Cl_2) δ [ppm] = 8.23 – 8.18 (m, 2H, H-k), 8.15 (d, *J* = 8.7 Hz, 1H, H-c), 7.86 (d, *J* = 8.6 Hz, 1H, H-b), 7.52 – 7.46 (m, 2H, H-l), 7.45 – 7.36 (m, 2H, H-f, H-m), 7.26 (dd, *J* = 8.1, 1.5 Hz, 1H, H-e), 7.09 (dd, *J* = 7.5, 1.5 Hz, 1H, H-g), 2.64 (s, 12H, H-o).

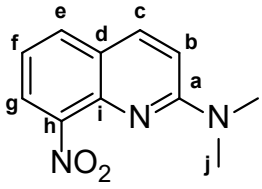
^{13}C NMR (101 MHz, CD_2Cl_2) δ [ppm] = 162.8 (C-n), 154.0 (C-a), 151.5 (C-h), 142.2 (C-i), 140.1 (C-j), 137.2 (C-c), 129.2 (C-m), 128.9 (C-l), 128.5 (C-d), 127.8 (C-f), 127.3 (C-k), 120.1 (C-g), 117.9 (C-e), 117.8 (C-b), 39.7 (C-o).

HR-ESI-MS: $[M+H]^+$ (m/z (%) $[M+H]^+$, M+H = $C_{20}H_{23}N_4$) found: 319.19151 (100), 320.19466 (22), 321.19780 (2). Calculated: 319.19172 (100), 320.19508 (22), 321.19843 (2).

IR (ATR, ṽ) = 3055 (w), 3046 (w), 3019 (w), 3015 (w), 2990 (w), 2930 (w), 2876 (w), 2864 (w), 2845 (w), 2814 (vw), 2806 (vw), 2791 (w), 1618 (w), 1584 (s), 1564 (vs), 1541 (vs), 1506 (vs), 1487 (vs), 1472 (s), 1456 (vs), 1429 (vs), 1420 (vs), 1400 (m), 1381 (vs), 1366 (vs), 1348 (s), 1319 (m), 1302 (w), 1285 (m), 1234 (w), 1223 (s), 1186 (w), 1161 (w), 1140 (vs), 1109 (w), 1090 (m), 1061 (m), 1013 (vs), 999 (m), 957 (w), 939 (w), 924 (w), 889 (w), 853 (w), 839 (vs), 820 (w), 779 (vs), 766 (vs), 756 (vs), 710 (s), 698 (s), 677 (s), 638 (vw), 627 (w), 619 (w), 583 (vw), 573 (w), 552 (w), 532 (vw), 505 (w), 476 (w), 467 (vw), 457 (w), 420 (w) cm^{-1}.

2.2 Synthesis of TMG2NMe$_2$qu and corresponding precursors

2.2.1 Synthesis of 8-nitro-2-dimethylaminequinoline



217.23 g/mol

A pressure flask (100 mL) was charged with 2-chloro-8-nitroquinoline (8.00 g, 38.4 mmol, 1.00 equiv.), *N*-methylmethanamine hydrochloride (18.8 g, 230 mmol, 6.00 equiv.), water (37.0 mL) and ethanol (7.30 mL). Subsequently, sodium hydroxide (9.20 g, 230 mmol, 6.00 equiv.) was added to the mixture and the flask was sealed tight. The reaction mixture was then stirred and heated to 130 °C; a blast-panel placed in front of the reaction as a safety measure. After 4 hours, the initial yellow reaction had turned red and was allowed to cool to room temperature. The aqueous phase was extracted with dichloromethane (4x 50 mL), the organic phase was separated and dried over Na_2SO_4, and the remaining solvent was reduced under reduced pressure. The remaining solution was subsequently filtered over alumina and the remaining solvent was removed under reduced pressure. The remaining yellow solid was dried

in-vacuo and the product 8-nitro-2-dimethylaminequinoline (8.30 g, 38.2 mmol, 100% yield) was obtained as a yellow solid without further purification. The product needs to be stored under inert conditions to prevent decomposition.

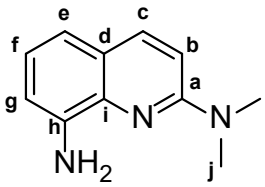
^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm] = 7.91 – 7.81 (m, 2H, H-c, H-g), 7.71 (dd, *J* = 7.9, 1.5 Hz, 1H, H-e), 7.13 (t, *J* = 7.8 Hz, 1H, H-f), 6.93 (d, *J* = 9.3 Hz, 1H, H-b), 3.22 (s, 6H, H-j).

^{13}C NMR (101 MHz, $CDCl_3$) δ [ppm] = 158.1 (C-a), 145.4 (C-h), 140.2 (C-i), 137.0 (C-c), 131.6 (C-e), 124.5 (C-g), 123.9 (C-d), 119.4 (C-f), 110.5 (C-b), 37.9 (C-j).

HR-ESI-MS: $[M+H]^+$ (m/z (%) $[M+H]^+$, M+H = $C_{11}H_{12}N_3O_2$) found: 218.09157 (100), 219.09471 (13), 220.09705 (1). Calculated: 218.09240 (100), 219.09576 (12), 220.09665 (1).

IR (ATR, ṽ) = 3075 (vw), 3046 (vw), 3007 (vw), 2936 (w), 2887 (vw), 2880 (vw), 2797 (vw), 1620 (vs), 1609 (s), 1520 (vs), 1489 (m), 1443 (m), 1427 (s), 1402 (w), 1387 (vs), 1352 (vs), 1333 (vs), 1236 (m), 1215 (w), 1179 (w), 1157 (vs), 1105 (w), 1070 (w), 1063 (w), 1026 (w), 1011 (vw), 978 (m), 961 (w), 922 (vw), 874 (m), 862 (m), 827 (vs), 802 (s), 795 (s), 768 (vs), 735 (m), 673 (w), 656 (s), 598 (vw), 552 (vw), 530 (w), 513 (w), 505 (w), 455 (w) cm^{-1}.

2.2.2 Synthesis of 2-*N*,2-*N*-dimethylquinoline-2,8-diamine



187.25 g/mol

A 500 mL Schlenk-flask was flushed with nitrogen and evacuated three times in a row. Afterwards, 2-chloro-8-nitroquinoline (5.00 g, 23.0 mmol, 1.00 equiv.) and palladium on charcoal (141 mg, 10 wt-%, 1.32 mmol, 0.0576 equiv.) were added in nitrogen counterflow. After the flask was evacuated and flushed with nitrogen three times, the powder in the flask was allowed to settle before methanol (230 mL) was slowly added under nitrogen counterflow. The pressure inside was reduced until the solvent started to boil and then flushed with nitrogen. Then, the nitrogen atmosphere was substituted with hydrogen using balloons. Afterwards, the reaction was stirred at room temperature for 5 hours with the hydrogen balloons attached. Afterwards, the solvent was removed under reduced pressure, the crude product was dissolved in dichloromethane (100 mL) and filtered through silica to remove the catalyst. The remaining solvent was removed under reduced pressure and after drying *in-vacuo*, 2-*N*,2-*N*-dimethylquinoline-2,8-diamine (4.17 g, 22.3 mmol, 97% yield) was obtained as a yellow solid

without further purification. The product needs to be stored under inert conditions to prevent decomposition.

^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm] = 7.82 (d, *J* = 9.1 Hz, 1H, H-c), 7.06 – 6.98 (m, 2H, H-e, H-g), 6.92 – 6.83 (m, 2H, H-b, H-f), 4.70 (s, 2H, H-N), 3.21 (s, 6H, H-j).

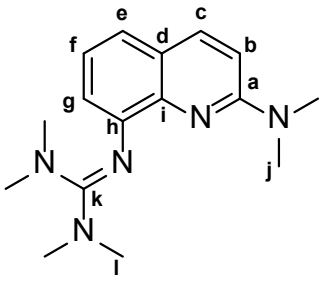
^{13}C NMR (101 MHz, $CDCl_3$) [ppm] = δ 156.3 (C-a), 141.6 (C-i), 137.7 (C-h), 137.5 (C-c), 122.3 (C-d), 122.1 (C-e/C-g), 116.3 (C-e/C-g), 111.0 (C-f), 109.3 (C-b), 38.3 (C-j).

HR-ESI-MS: $[M+H]^+$ (m/z (%) $[M+H]^+$, M+H = $C_{11}H_{14}N_3$) found: 188.11782 (100), 189.12108 (11). Calculated: 188.11822 (100), 189.12158 (12), 190.12493 (1).

IR (ATR, ṽ) = 3412 (w), 3316 (w), 3049 (w), 3021 (vw), 2924 (w), 2841 (w), 2187 (vw), 2160 (vw), 2039 (vw), 1919 (vw), 1883 (vw), 1736 (vw), 1618 (vs), 1605 (vs), 1560 (s), 1514 (vs), 1499 (vs), 1491 (s), 1447 (s), 1427 (vs), 1402 (w), 1377 (vs), 1344 (m), 1335 (s), 1279 (s), 1242 (m), 1186 (w), 1171 (w), 1148 (s), 1132 (w), 1076 (w), 1059 (w), 978 (m), 961 (w), 856 (w), 818 (vs), 795 (m), 741 (vs), 704 (m), 662 (m), 557 (w), 548 (w), 517 (w), 474 (w), 467 (w), 424 (vw), 415 (vw) cm^{-1}.

2.2.3 Synthesis of TMG2NMe$_2$qu

The guanidine synthesis was performed following a slightly modified procedure of Herres-Pawlis et al. which bases on the procedure of Kantlehner et al.[3b, 17]



285.40 g/mol

2-*N*,2-*N*-dimethylquinoline-2,8-diamine (3.78 g, 20.2 mmol, 1.00 equiv.) and TMG-VS (3.85 g, 22.5 mmol, 1.11 equiv.) were dissolved in acetonitrile (80.0 mL) and triethylamine (5.68 g, 7.78 mL, 56.1 mmol, 2.78 equiv.) was added. The reaction mixture was heated to reflux for 1 hour under stirring and subsequently allowed to cool to room temperature. An aqueous KOH solution (70 mL, 50 wt-%) was added to the reaction mixture and the aqueous phase was extracted with acetonitrile (3x 50 mL). The organic layer was separated, dried over Na_2SO_4 and the remaining solvent was removed under reduced pressure. The remaining brown oil was then dissolved in small amounts of DCM and filtered through alumina with DCM as eluent, after which the solvent was removed under reduced pressure. The resulting oil was then heated under vacuum (<10^{-1} mbar), starting at 100 °C and rising to 250 °C, to remove any remaining urea derivative. TMG2NMe$_2$qu (5.00 g, 17.5 mmol, 87%

yield) was obtained as a brown oil that slowly solidifies in several weeks. The product needs to be stored under inert conditions to avoid protonation.

^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm] = 7.79 (d, *J* = 9.0 Hz, 1H, H-c), 7.10 – 7.04 (m, 3H, H-e, H-f, H-g), 6.78 (d, *J* = 9.0 Hz, 1H, H-b), 3.10 (s, 6H, H-j), 2.64 (s, 12H, H-l).

^{13}C NMR (101 MHz, $CDCl_3$) δ [ppm] = 162.0 (C-k), 156.6 (C-a), 147.7 (C-h), 141.3 (C-i), 137.6 (C-c), 123.0 (C-d), 122.4 (C-e/C-f/C-g), 120.8 (C-e/C-f/C-g), 118.5 (C-e/C-f/C-g), 108.1 (C-b), 39.5 (C-l), 37.8 (C-j).

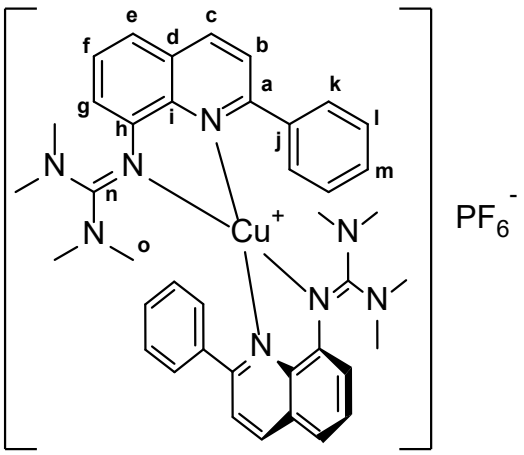
HR-ESI-MS: $[M+H]^+$ (m/z (%) $[M+H]^+$, M+H = $C_{16}H_{24}N_5$) found: 286.20252 (100), 287.20553 (18), 288.20857 (2). Calculated: 286.20262 (100), 287.20598 (17), 288.20933 (1).

IR (ATR, ṽ) = 3048 (vw), 2997 (vw), 2926 (w), 2874 (w), 2847 (w), 2816 (w), 2789 (vw), 1611 (vs), 1570 (vs), 1553 (vs), 1501 (vs), 1462 (s), 1454 (s), 1437 (vs), 1423 (vs), 1400 (s), 1375 (vs), 1360 (vs), 1323 (m), 1306 (m), 1275 (w), 1225 (m), 1215 (s), 1177 (m), 1140 (vs), 1109 (w), 1080 (m), 1061 (m), 1053 (s), 1011 (vs), 974 (m), 959 (w), 945 (vw), 926 (w), 881 (w), 856 (w), 831 (s), 826 (vs), 806 (w), 799 (s), 752 (vs), 745 (vs), 712 (w), 681 (m), 665 (m), 621 (w), 569 (w), 519 (w), 501 (vw), 459 (w) cm^{-1}.

2.3 Synthesis of Complexes

2.3.1 Synthesis of $[Cu(TMG2Phqu)_2]PF_6 \cdot CH_2Cl_2$ (C1-PF6)

A preheated Schlenk flask was charged with $[Cu(MeCN)_4]PF_6$ (250 mg, 671 µmol, 1.00 equiv.) and TMG2Phqu (450 mg, 1.41 mmol, 2.11 equiv.) in a nitrogen counterflow. The solids were dissolved in dichloromethane (3.00 mL) and stirred for 30 min at 28 °C. Afterwards, pentane was added to the mixture and the resulting black precipitate was filtered off under reduced pressure. The product was washed with pentane (3x 10 mL) and dried *in-vacuo*. $[Cu(TMG2Phqu)_2]PF_6 \cdot CH_2Cl_2$ (390 mg, 461 µmol, 69% yield) was obtained as a brown powder.



845.35 g/mol

The solid state structure was obtained by dissolving **C1-PF_6** (42.3 mg, 5 µmol) in DCM (2 mL) inside a Schlenk tube and layering the resulting solution with pentane. The crystals were obtained the following day.

Due to the broad signals, the NMRs could not be completely assigned.

^{1}H NMR (400 MHz, CD_3CN) δ [ppm] = 8.32 (d, *J* = 6.1 Hz, 2H, H-c), 7.94 – 7.64 (m, 6H, H-e/H-l), 7.49 – 7.40 (m, 4H, H-f/H-m), 7.19 – 6.87 (m, 6H, H-g/H-k), 6.72 (d, *J* = 6.9 Hz, 2H, H-b), 2.41 (s, 24H, H-o).

^{13}C NMR (101 MHz, CD_3CN) δ [ppm] = 163.8 (C-n), 156.0 (C_q), 148.7 (C_q), 142.4 (C_q), 141.4 (C_q), 138.4 (C-c), 129.8 (C-g/C-k), 129.5 (C-g/C-k), 128.8 (C-f/C-m), 128.5 (C-e/C-l, C-d) , 123.4 (C-e/C-l), 119.5 (C-f/C-m), 119.1 (C-b), 39.8 (C-o).

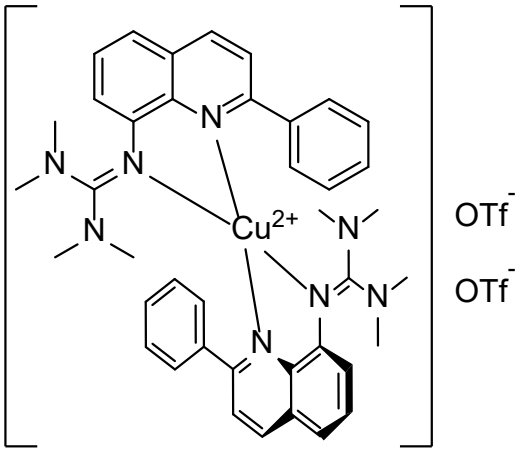
HR-ESI-MS: M^+ (m/z (%) $[M]^+$, M = $C_{40}H_{44}N_8Cu$) found: 699.29711 (100), 700.29982 (45), 701.29611 (50), 702.29792 (20). Calculated: 699.29794 (100), 700.301297 (43), 701.29613 (45), 702.29949 (19).

IR (ATR, $\tilde{\nu}$) = 3055 (vw), 2930 (vw), 2886 (vw), 2870 (vw), 2801 (vw), 2160 (vw), 2035 (vw), 1736 (vw), 1595 (vw), 1578 (vw), 1524 (s), 1489 (w), 1470 (w), 1454 (m), 1422 (m), 1406 (m), 1393 (s), 1369 (w), 1341 (w), 1323 (w), 1285 (w), 1273 (w), 1231 (w), 1153 (w), 1107 (vw), 1094 (w), 1084 (w), 1065 (w), 1016 (w), 926 (vw), 899 (vw), 876 (w), 831 (vs), 766 (m), 756 (m), 696 (m), 642 (w), 617 (vw), 584 (vw), 555 (vs), 525 (w), 478 (w), 463 (w), 459 (w), 444 (w), 430 (vw), 424 (vw), 419 (vw), 409 (vw) cm^{-1}.

XRD: XRD: See Fig. S1, Table S2.

2.3.2 Synthesis of $[Cu(TMG2Phqu)_2](OTf)_2 \cdot 0.5\ H_2O$ (C2-OTf)

A vial was charged with TMG2Phqu (261 mg, 820 µmol, 2.09 equiv.) and $[Cu(MeCN)_4](OTf)_2$ (206 mg, 392 µmol, 1.00 equiv.) and dissolved in absolute dichloromethane (5.00 mL). The solution was stirred at 28 °C for 10 minutes, after which the complex was precipitated via hexane. The resulting precipitate was filtered off and dissolved in DCM (2 mL) and pipetted into a beaker of pentane (50 mL), the resulting powder was filtered off under reduced pressure and dried *in-vacuo*. $[Cu(TMG2Phqu)_2](OTf)_2 \cdot 0.5\ H_2O$ (109 mg, 109 µmol, 28% yield) was obtained as a black powder.



998.52 g/mol

The solid state structure was obtained by dissolving **C2-OTf** (50 mg, 5 µmol) in MeCN (2 mL) inside a Schlenk tube and layering the resulting solution with diethyl ether. The crystals were obtained the following week.

HR-ESI-MS: $[TMG2Phqu-NMe_2]^+$ ((m/z (%) $[M]^+$, M = $C_{18}H_{16}N_3$) found: 274.13437. Calculated: 274.13387

$[TMG2Phqu+H]^+$ ((m/z (%) $[M+H]^+$, M+H = $C_{20}H_{23}N_4$) found: 319.19138. Calculated: 319.19151.

$[\{Cu(TMG2Phqu)\}OTf]^+$ ((m/z (%) $[M]^+$, M = $C_{21}H_{22}CuF_3N_4O_3S$) found: 530.06647 (100), 531.07007 (20), 532.06549 (45), 533.06802 (10). Calculated: 530.06552 (100), 531.06888 (23), 532.06371 (45), 533.06707 (10).

$[Cu(TMG2Phqu)_2]^+$ (m/z (%) $[M]^+$, M = $C_{40}H_{44}N_8Cu$) found: 699.29958 (100), 700.30306 (45), 701.29728 (50), 702.30110 (20). Calculated: 699.29794 (100), 700.301297 (43), 701.29613 (45), 702.29949 (19).

$[\{Cu(TMG2Phqu)_2\}OTf]^+$ (m/z (%) $[M]^+$, M = $C_{41}H_{44}CuF_3N_8O_3S$) found: 848.25230 (100), 849. 25579 (43), 850.24961 (43), 851.XYZ (18), 852.25845 (5). Calculated: 848.24997 (100), 849.25332 (44), 850.24816 (45), 851.25151 (20), 852.25487 (4).

[{Cu(TMG2Phqu)$_2$}$_2$OTf$_3$]$^+$ ((m/z (%) [M]$^+$, M = $C_{83}H_{88}Cu_2F_9N_{16}O_9S_3$) found: 1845.45567 (60) 1846.45870 (65), 1847.45565 (100), 1848.45756 (80), 1849.45636 (50), 1850.45673 (27), 1851.45718 (14). Calculated: 1845.45207 (74), 1846.45535 (72), 1847.45306 (100), 1848.45448 (81), 1849.45405 (54), 1850.45362 (32), 1851.45504 (15), 1852.45460 (6).

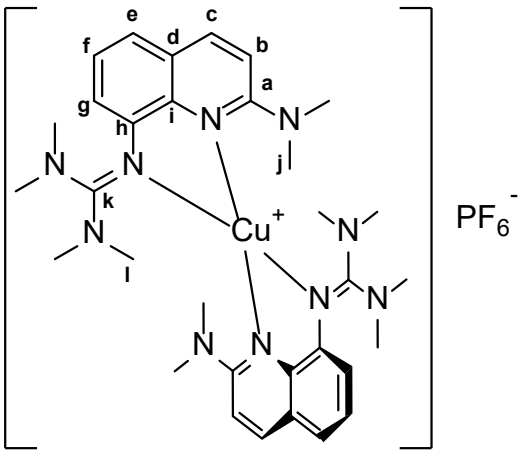
IR (ATR, ṽ) = 2926 (vw), 2183 (vw), 2160 (vw), 2039 (vw), 1626 (vw), 1582 (m), 1558 (w), 1520 (m), 1510 (m), 1491 (w), 1476 (w), 1460 (m), 1435 (w), 1427 (w), 1404 (s), 1385 (w), 1339 (w), 1319 (w), 1260 (vs), 1225 (vs), 1152 (vs), 1144 (vs), 1099 (w), 1084 (w), 1061 (vw), 1028 (vs), 1001 (w), 922 (vw), 918 (vw), 897 (vw), 864 (w), 833 (w), 808 (vw), 756 (s), 710 (w), 696 (m), 637 (vs), 571 (w), 544 (vw), 515 (m), 482 (w), 424 (vw), 419 (w) cm^{-1}.

XRD: See Fig. S2, Table S2.

PXRD: See Fig. S7.

2.3.3 Synthesis of [Cu(TMG2NMe$_2$qu)$_2$]PF$_6$ · 2 CH$_2$Cl$_2$ (C3-PF$_6$· DCM)

Inside a glove box, a 20 mL vial was charged with TMG2NMe$_2$qu (1.00 g, 3.50 mmol, 2.10 equiv.) and [Cu(MeCN)$_4$]PF$_6$ (622 mg, 1.67 mmol, 1.00 equiv.). The solids were dissolved in dichloromethane (4.00 mL) and pentane was allowed to diffuse into the solution for a week. Afterwards, black column-like crystals could be filtered off and dried *in vacuo*. [Cu(TMG2NMe2qu)$_2$]PF$_6$ PF$_6$ · 2 CH$_2$Cl$_2$ (1.30 g, 1.62 mmol, 97% yield, 97% purity) was obtained in the form of brown crystals.



779.30 g/mol

^{1}H NMR (400 MHz, CD$_3$CN) δ]ppm] = 7.96 (d, *J* = 8.6 Hz, 2H, H-c), 7.26 (dd, *J* = 7.9, 1.4 Hz, 2H, H-e), 7.11 (t, *J* = 7.7 Hz, 2H, H-f), 7.02 (br. s, 2H, H-g), 6.63 (d, *J* = 7.5 Hz, 2H, H-b), 3.26 (s, 12H, H-j), 2.41 (s, 24H, H-l).

^{13}C NMR (101 MHz, CD$_3$CN) δ [ppm] = 164.3 (C-k), 157.5 (C-a), 145.6 (C-h), 142.2 (C-i), 138.8 (C-c), 124.3 (C-d), 123.3 (C-f), 121.0 (C-e), 119.6 (C-b), 111.8 (C-g), 40.0 (C-j, C-l).

HR-ESI-MS: $[Cu(TMG2NMe_2qu)_2]^+$ (m/z (%) $[M]^+$, M = $C_{32}H_{46}N_{10}Cu$) found: 633.32126 (100), 634.32478 (35), 635.31935 (46), 636.32294 (15), 637.32662 (1). Calculated: 633.31974 (100), 634.32310 (35), 635.31793 (45), 636.32129 (15), 637.32464 (3).

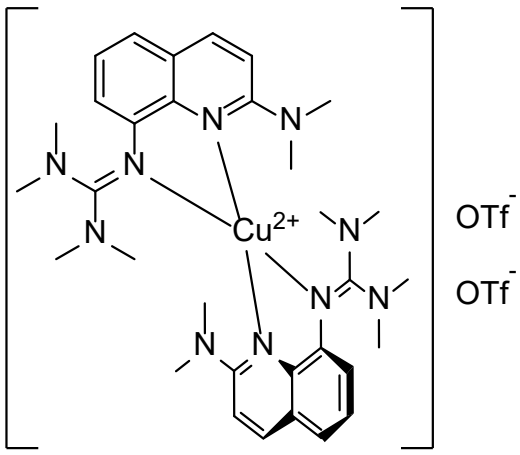
$[Cu(TMG2NMe_2qu)_2-C_{16}H_{23}N_5]^+$ (m/z (%), $[M]^+$, M = $C_{16}H_{23}N_5Cu$) found: 348.12544 (100), 349.12848 (17), 350.12350 (47), 351.12648 (5), 352.12955 (<1). Calculated: 348.12440 (100), 349.13067 (17), 350.12260 (45), 351.12594 (8), 352.12930 (1).

IR (ATR, ṽ) = 3049 (vw), 3003 (vw), 2928 (vw), 2886 (vw), 2878 (vw), 2868 (vw), 2803 (vw), 2374 (vw), 2166 (vw), 2029 (vw), 2018 (vw), 1981 (vw), 1616 (w), 1599 (w), 1522 (vs), 1518 (vs), 1489 (w), 1470 (m), 1441 (m), 1422 (s), 1408 (m), 1391 (s), 1383 (s), 1364 (m), 1348 (w), 1339 (m), 1271 (w), 1236 (w), 1223 (w), 1180 (w), 1153 (m), 1111 (vw), 1082 (vw), 1065 (w), 1018 (m), 980 (w), 930 (vw), 876 (w), 833 (vs), 791 (m), 752 (m), 710 (w), 694 (w), 673 (vw), 638 (w), 575 (w), 555 (vs), 523 (w) cm^{-1}.

XRD: See Fig. S3, Table S3.

2.3.4 Synthesis of $[Cu(TMG2NMe_2qu)_2](OTf)_2$ (C4-OTf)

To a solution of $TMG2NMe_2qu$ (31.0 mg, 109 µmol, 2.20 equiv.) in DCM (1 mL) a solution of $[Cu(MeCN)_4](OTf)_2$ (26.0 mg, 49.4 µmol, 1.00 equiv.) in MeCN (1 mL) was added, resulting in an immediate blackening of the mixture. By slow diffusion of Et_2O, the compound $[Cu(TMG2NMe_2qu)_2](OTf)_2$ crystallized after a few days in the form of black crystals.



932.46 g/mol

XRD: See Fig. S4, Table S3.

EPR: See Fig. S

3 Solid State Structures

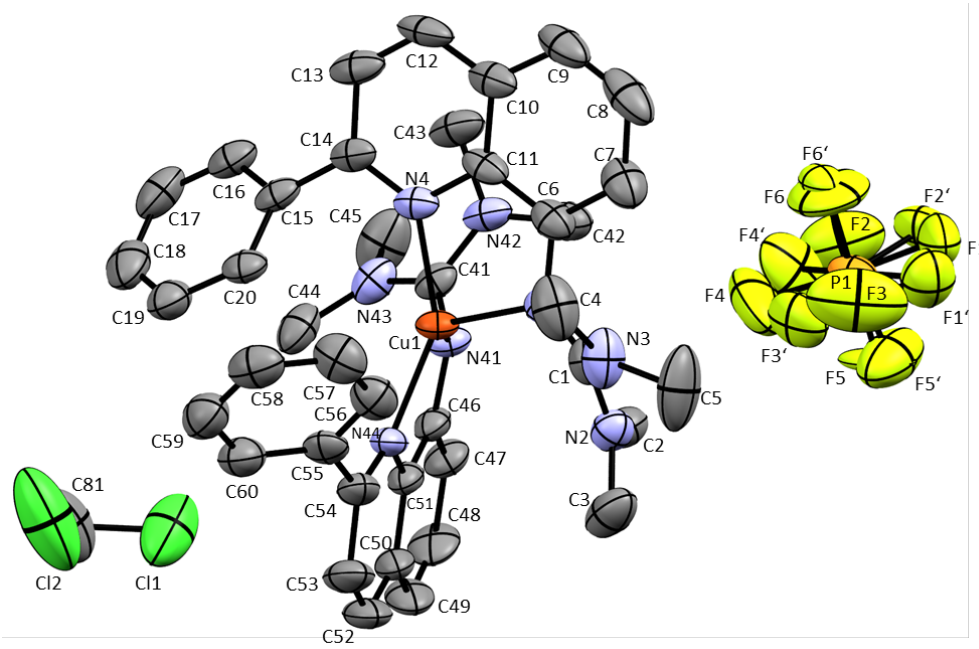


Figure S1: Molecular structure of $[Cu(TMG2Phqu)_2]PF_6 \cdot CH_2Cl_2$ (**C1-PF$_6$**) in the solid state (50 % probability, asymmetric unit, H atoms are omitted for clarity).

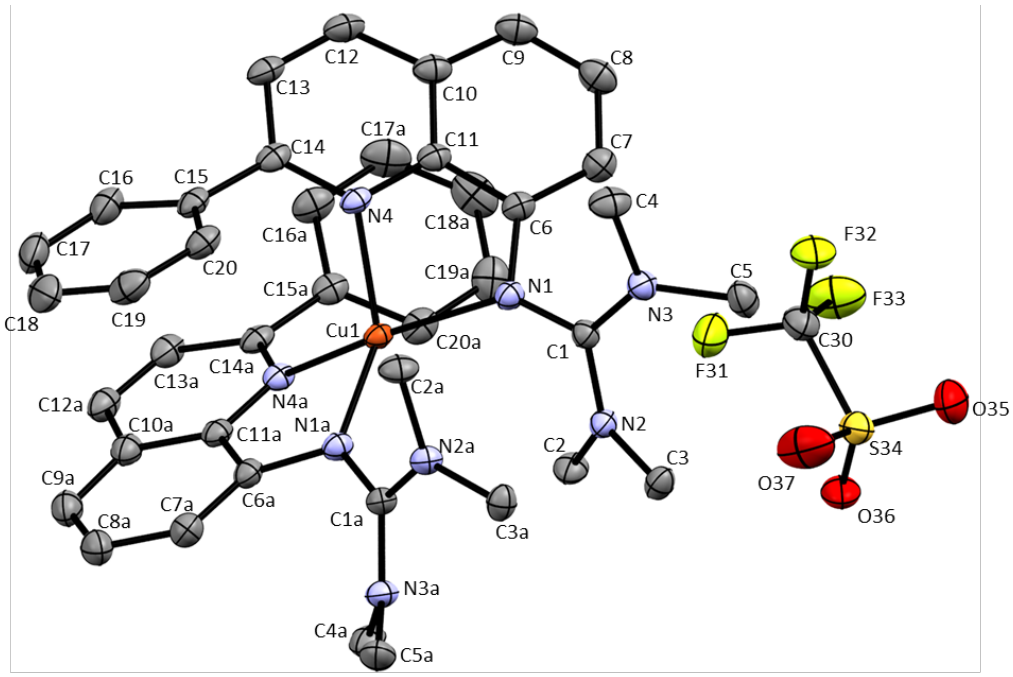


Figure S2: Molecular structure of $[Cu(TMG2Phqu)_2](OTf)_2 \cdot 0.5\ H_2O$ (**C2-OTf**) in the solid state (50 % probability, H atoms are omitted for clarity, H_2O masked with Squeeze.[13]

Table S2: Crystallographic data of $[Cu(TMG2Phqu)_2]PF_6 \cdot CH_2Cl_2$ (**C1-PF$_6$**) and $[Cu(TMG2Phqu)_2](OTf)_2 \cdot 0.5\ H_2O$ (**C2-OTf**). In **C2-OTf**, it was not possible to model the disordered solvent molecules (H_2O) in an adequate manner, and the data set was treated with the SQUEEZE routine as implemented in PLATON.[13]

	$[Cu(TMG2Phqu)_2]PF_6 \cdot CH_2Cl_2$ (**C1-PF$_6$**)	$[Cu(TMG2Phqu)_2](OTf)_2 \cdot 0.5\ H_2O$ (**C2-OTf**)
Empirical formula	$C_{41}H_{46}Cl_2CuF_6N_8P$	$C_{42}H_{44}CuF_6N_8O_6S_2$ [+ 0.5 H_2O]
Formular weight [g mol^{-1}]	930.27	998.51
Crystal size [mm]	0.130 x 0.120 x 0.100	0.160 x 0.120 x 0.050
Crystal system	monoclinic	Orthorhombic
Space group	$P2_1/c$	*Pbcn*
a [Å]	15.993(3)	12.985(3)
b [Å]	16.367(3)	22.954(5)
c [Å]	16.176(3)	14.661(3)
α [°]	90	90
β [°]	91.43(3)	90
γ [°]	90	90
V [Å^3]	4232.9(15)	4370.0(15)
Z	4	4
ρ [g cm^{-3}]	1.460	1.518
μ [mm^{-1}]	0.748	0.679
Wavelength[Å]	0.71073	0.71073
T [K]	150	100
F(000)	1920	2060
hkl range	$-19 \leq h \leq 19$, $-19 \leq k \leq 19$, $-19 \leq l \leq 19$	$-16 \leq h \leq 16$, $-29 \leq k \leq 27$, $-18 \leq l \leq 18$
Reflections collected	90187	46030
Independent reflections	7880	4774
$R_{int.}$	0.0911	0.0414
Number of parameters	595	298
Goodness-of-fit für F^2	1.052	1.047
R_1 [$I > 2\sigma(I)$]	0.0686	0.0421
wR_2 (all data)	0.2139	0.1206
Largest diff. Peak, hole [e Å^{-3}]	2.139, -1.168	0.779, -0.424

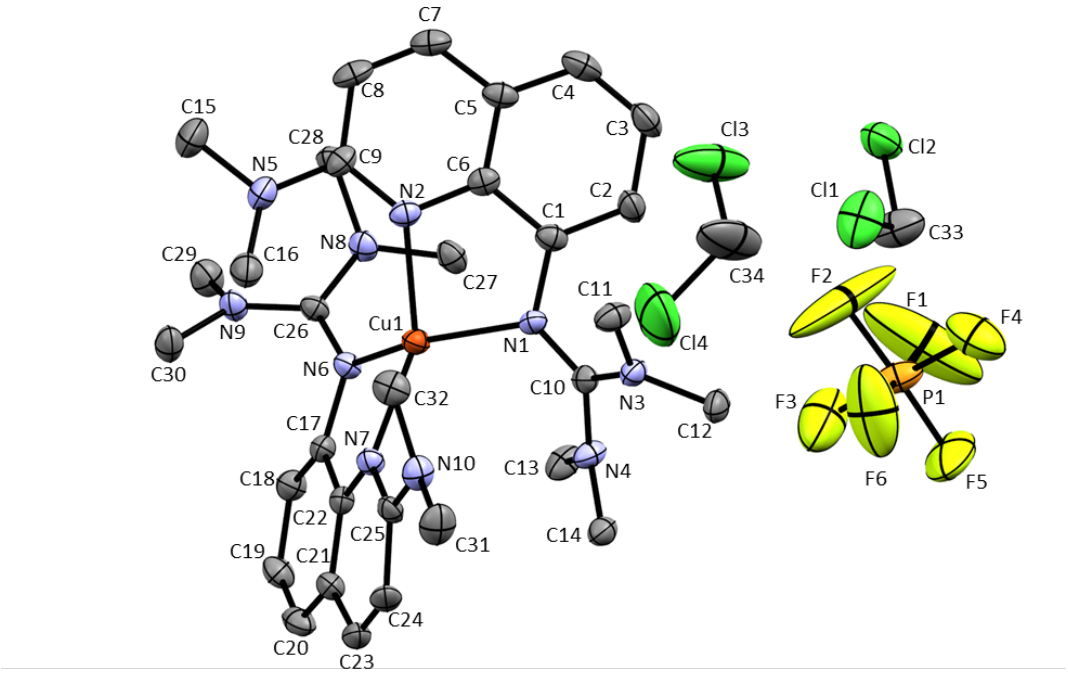


Figure S3: Molecular structure of $[Cu(TMG2NMe_2qu)_2]PF_6 \cdot 2\ CH_2Cl_2$ (**C3-PF$_6$**) in the solid state (50 % probability, asymmetric unit, H atoms are omitted for clarity). **C3-PF$_6$** is a twin and the data set was treated with the TwinRotMat routine as implemented in PLATON (rotation axis in reciprocal space (2 -1 0), twin law 1 0 0 -1 -1 0 0 0 -1).[13]

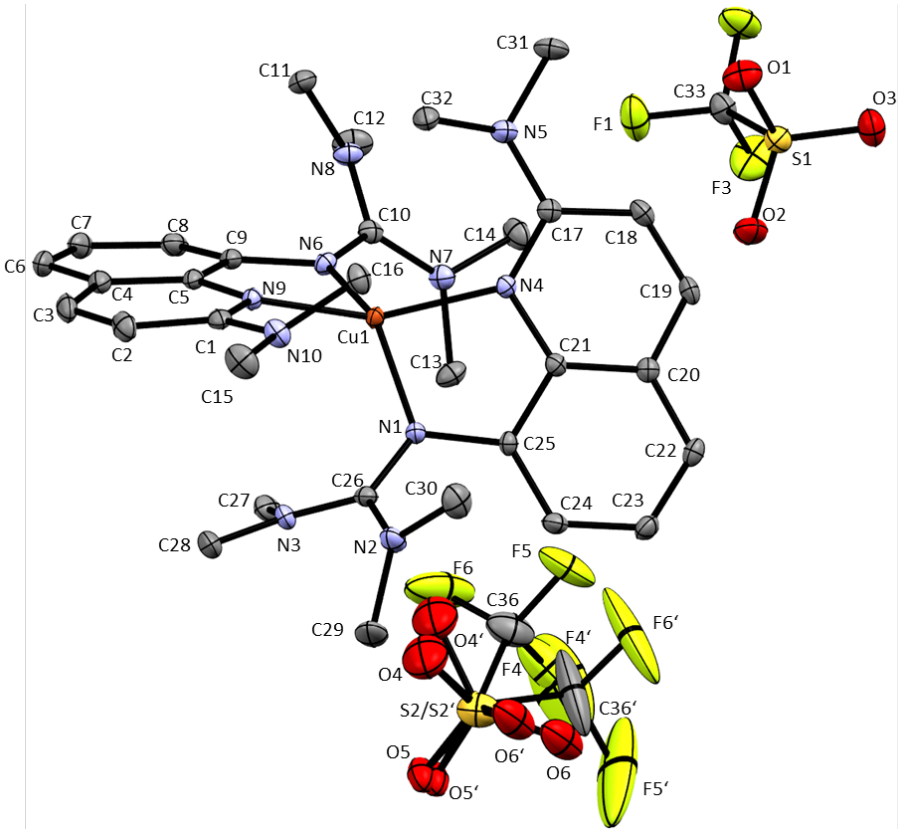


Figure S4: Molecular structure of $[Cu(TMG2NMe_2qu)_2](OTf)_2$ (**C4-OTf**) in the solid state (50 % probability, asymmetric unit, H atoms are omitted for clarity).

Table S3: Crystallographic data of $[Cu(TMG2NMe_2qu)_2]PF_6 \cdot 2\ CH_2Cl_2$ (**C3-PF$_6$**) and $[Cu(TMG2NMe_2qu)_2](OTf)_2$ (**C4-OTf**). **C3-PF$_6$** is a twin and the data set was treated with the TwinRotMat routine as implemented in PLATON (rotation axis in reciprocal space (2 -1 0), twin law 1 0 0 -1 -1 0 0 0 -1).[13]

	$[Cu(TMG2NMe_2qu)_2]PF_6 \cdot 2\ CH_2Cl_2$ (**C3-PF$_6$**)	$[Cu(TMG2NMe_2qu)_2](OTf)_2$ (**C4-OTf**)
Empirical formula	$C_{34}H_{50}Cl_4CuF_6N_{10}P \cdot 2\ CH_2Cl_2$	$C_{34}H_{46}CuF_6N_{10}O_6S_2$
Formular weight [g mol^{-1}]	949.15	932.47
Crystal size [mm]	0.113 x 0.100 x 0.057	0.170 x 0.160 x 0.085
Crystal system	trigonal	triclinic
Space group	$P3_2$	$P\bar{1}$
a [Å]	11.3244(16)	11.037(2)
b [Å]	11.3244(16)	12.206(2)
c [Å]	28.398(6)	16.663(3)
α [°]	90	98.57(3)
β [°]	90	104.20(3)
γ [°]	120	108.83(3)
V [Å^3]	3154.0(11)	1995.1(8)
Z	3	2
ρ [g cm^{-3}]	1.499	1.552
μ [mm^{-1}]	0.878	0.738
Wavelength[Å]	0.71073	0.71073
T [K]	100	100
F(000)	1470	966
hkl range	$-17 \leq h \leq 8$, $-17 \leq k \leq 17$, $-43 \leq l \leq 43$	$-14 \leq h \leq 14$, $-15 \leq k \leq 16$, $-22 \leq l \leq 22$
Reflections collected	15567	39575
Independent reflections	15567	9590
$R_{int.}$	twin	0.0385
Number of parameters	518	599
Goodness-of-fit für F^2	0.871	1.108
R_1 [$I > 2\sigma(I)$]	0.0464	0.044
wR_2 (all data)	0.1094	0.1389
Largest diff. Peak, hole [e Å^{-3}]	1.031, -0.692	3.455, -0.623

Table S4: Key bond lengths, bond angles and structure parameters of the Cu(I) complex cations of $[Cu(TMG2Phqu)_2]PF_6 \cdot CH_2Cl_2$ (**C1-PF$_6$**), $[Cu(TMG2Phqu)_2](OTf)_2 \cdot 0.5\ H_2O$ (**C2-OTf**) $[Cu(TMG2NMe_2qu)_2]PF_6 \cdot 2\ CH_2Cl_2$ (**C3-PF$_6$**) and $[Cu(TMG2NMe_2qu)_2](OTf)_2$ (**C4-OTf**).

	C1-PF$_6$	**C2-OTf**	**C3-PF$_6$**	**C4-OTf**
		Bond Lengths [Å]		
$Cu–N_{gua,1}$	2.097(4)	1.982(2)	1.995(4)	1.964(2)
$Cu–N_{gua,2}$	2.086(4)	1.982(2)	1.991(4)	1.961(2)
$Cu–N_{qu,1}$	2.042(4)	2.0010(19)	2.164(4)	2.010(2)
$Cu–N_{qu,2}$	2.039(4)	2.0010(19)	2.155(4)	1.9922(19)
		Bond Angles [°]		
$N_{gua,1}$–Cu–$N_{gua,2}$	118.29(15)	119.69(11)	141.04(14)	141.60(8)
$N_{gua,1}$–Cu– $N_{qu,2}$	119.50(16)	143.56(8)	112.85(15)	105.67(9)
$N_{gua,1}$–Cu– $N_{qu,1}$	81.69(16)	82.70(8)	81.33(15)	84.07(9)
$N_{gua,2}$–Cu– $N_{qu,1}$	112.17(15)	143.56(8)	111.86(15)	106.62(9)
$N_{gua,2}$–Cu– $N_{qu,2}$	81.65(16)	82.769(8)	81.90(15)	84.12(8)
$N_{qu,1}$–Cu– $N_{qu,2}$	146.72(16)	95.23(11)	138.81(14)	149.10(8)
		Structure Parameters		
τ_4[a]	0.67	0.52	0.57	0.49
$\Delta\tau_4$	0.15		0.08	
$\emptyset\tau_4$	0.60		0.53	

[a] $\tau_4 = \frac{360° - \alpha - \beta}{141°}$.[18]

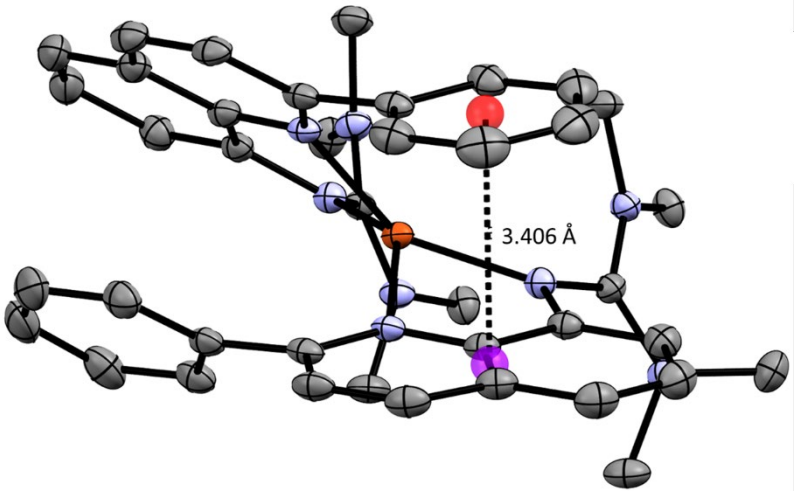


Figure S5: Image of the constructed centroids (red sphere) of the phenyl-substituent and the opposite-lying quinolinyl unit (magenta sphere) in **C2-OTf** and the measured distance between the two (H atoms are omitted for clarity).

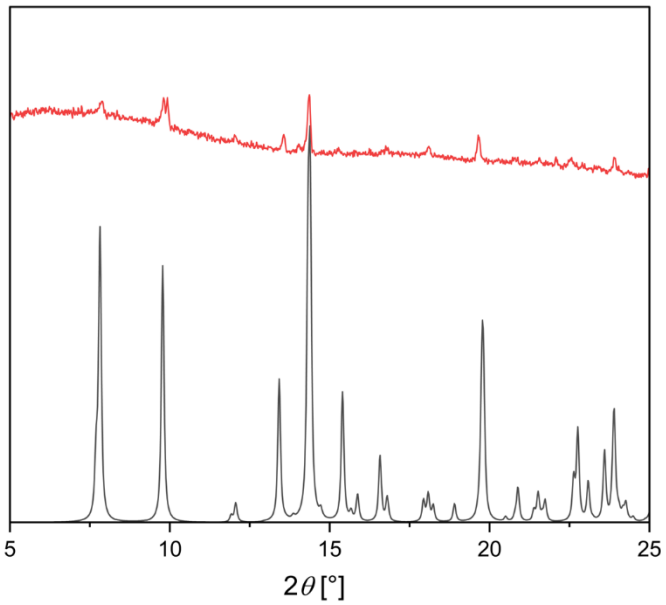


Figure S6: Experimental (red) and simulated (black) PXRD spectra of $[Cu(TMG2Phqu)_2](OTf)_2 \cdot 0.5\ H_2O$ (**C2-OTf**).

4 UV/Vis Spectra

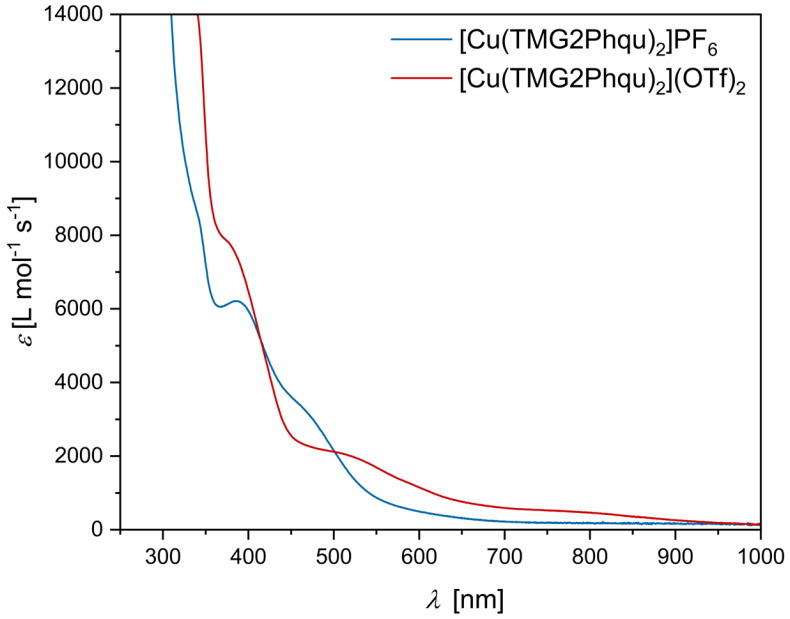


Figure S7: UV/Vis spectra of $[Cu(TMG2Phqu)_2]PF_6 \cdot CH_2Cl_2$ (**C1-PF$_6$**) and $[Cu(TMG2Phqu)_2](OTf)_2 \cdot 0.5\ H_2O$ (**C2-OTf**) (both with *c* = 1 mM) in MeCN solution at room temperature.

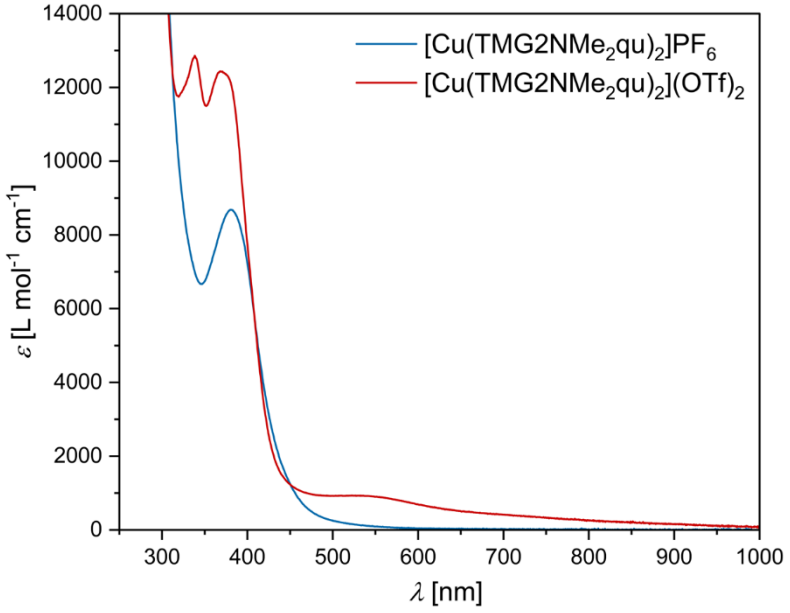


Figure S8: UV/Vis spectra of $[Cu(TMG2NMe_2qu)_2]PF_6 \cdot 2\ CH_2Cl_2$ (**C3-PF$_6$**) and $[Cu(TMG2NMe_2qu)_2](OTf)_2$ (**C4-OTf**) (both with *c* = 1 mM) in MeCN solution at room temperature.

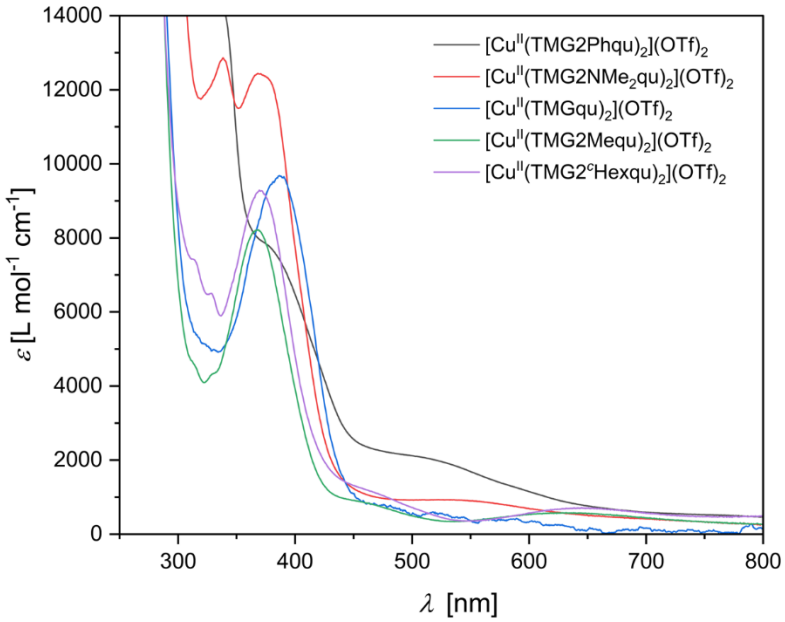


Figure S9: UV/Vis spectra of all herein discussed $[Cu^{II}(L)_2]$ complexes (c = 1 mM) in MeCN solution at room temperature. The spectra of $[Cu^{II}(TMGqu)_2](OTf)_2$, $[Cu^{II}(TMG2Mequ)_2](OTf)$ and $[Cu^{II}(TMG2^cHexqu)_2](OTf)$ were taken from Herres-Pawlis *et al.*[1]

5 Cyclic Voltammetry Measurements

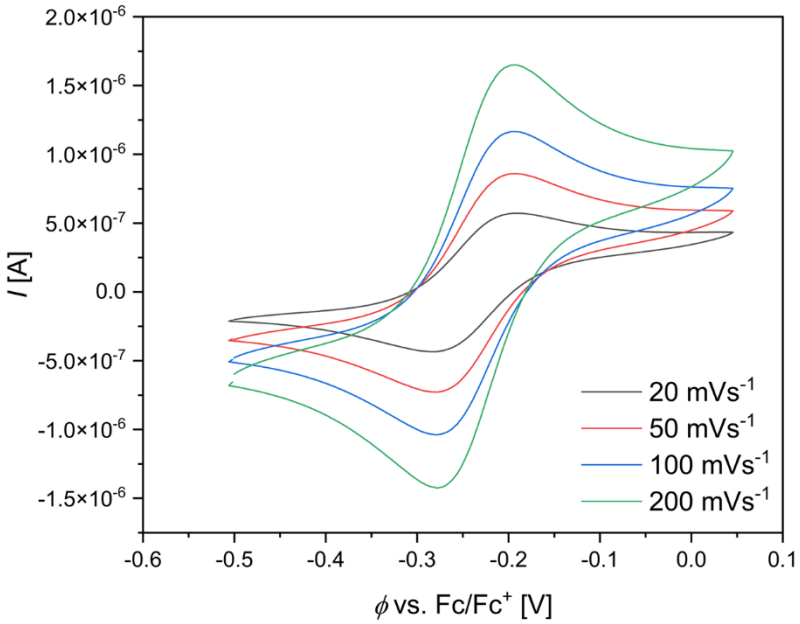


Figure S10: Cyclic voltammograms of the complex redox couple $[Cu(TMG2Phqu)_2]^{+/2+}$ (**R1**) starting from $[Cu(TMG2Phqu)_2]PF_6 \cdot CH_2Cl_2$ (**C1-PF$_6$**) (c = 1 mM) in MeCN with $[NBu_4][PF_6]$ (c = 0.1 M).

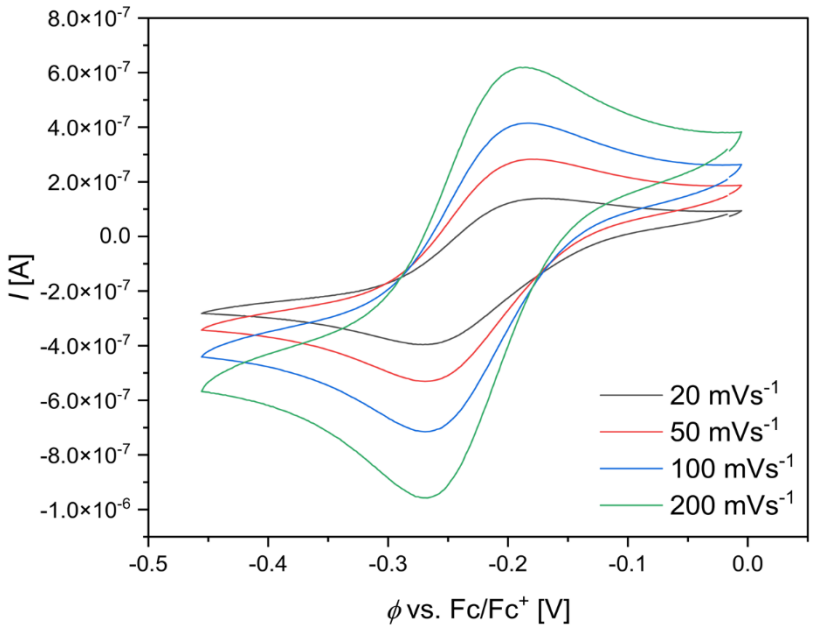


Figure S11: Cyclic voltammograms of the complex redox couple $[Cu(TMG2Phqu)_2]^{+/2+}$ (**R1**) starting from $[Cu(TMG2Phqu)_2](OTf)_2 \cdot 0.5\ H_2O$ (**C2-OTf**) (c = 1 mM) in MeCN with $[NBu_4][PF_6]$ (c = 0.1 M).

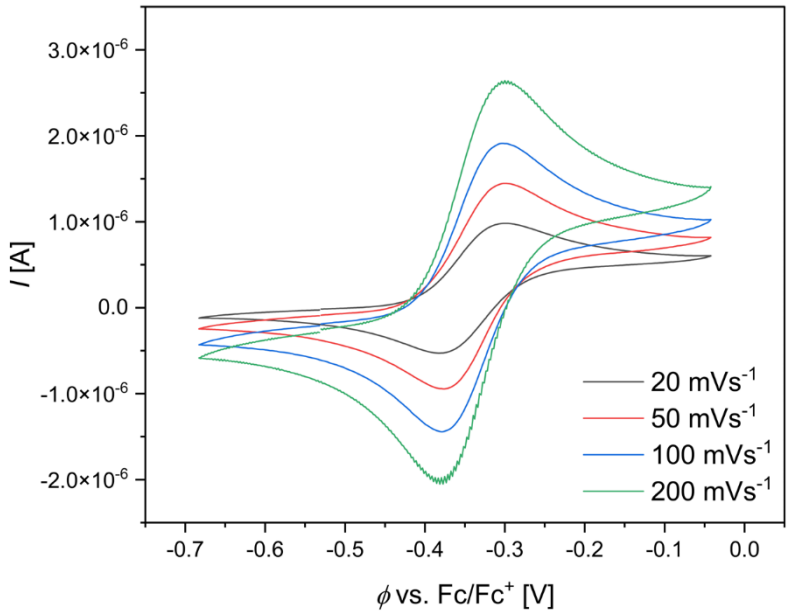


Figure S12: Cyclic voltammograms of the complex redox couple $[Cu(TMG2NMe_2qu)_2]^{+/2+}$ (**R2**) starting from $[Cu(TMG2NMe_2qu)_2]PF_6 \cdot 2\ CH_2Cl_2$ (**C3-PF$_6$**) (c = 1 mM) in MeCN with $[NBu_4][PF_6]$ (c = 0.1 M).

Table S5: Key parameters of the cyclic voltammograms of $[Cu(TMG2Phqu)_2]PF_6 \cdot CH_2Cl_2$ (**C1-PF$_6$**), $[Cu(TMG2Phqu)_2](OTf)_2 \cdot 0.5\ H_2O$ (**C2-OTf**) and $[Cu(TMG2NMe_2qu)_2]PF_6 \cdot 2\ CH_2Cl_2$ (**C3-PF$_6$**).

Sarting compound	$E_{1/2}$ [V] *vs.* Fc/Fc^+	ΔE_P [mV] mean	ΔE_P [mV] 20, 50, 100, 200 mV s^{-1}	I_{ox}/I_{red} [ ] mean	I_{ox}/I_{red} [ ] 20, 50, 100, 200 mV s^{-1}	$\Delta I_{ox}/I_{red}$ [ ] max vs. min
C1-PF$_6$	-0.239	70	72, 71, 69, 69	1.06	1.09, 1.06, 1.05, 1.04	0.05
C2-OTf	-0.220	66	67, 65, 65, 66	0.80	0.79, 0.81, 0.81, 0.82	0.03
C3-PF$_6$	-0.335	71	72,69, 71,72	1.06	1.04, 1.04, 1.09, 1.10	0.06

6 Kinetic Plots of the Stopped-Flow UV/vis Spectroscopic Measurements

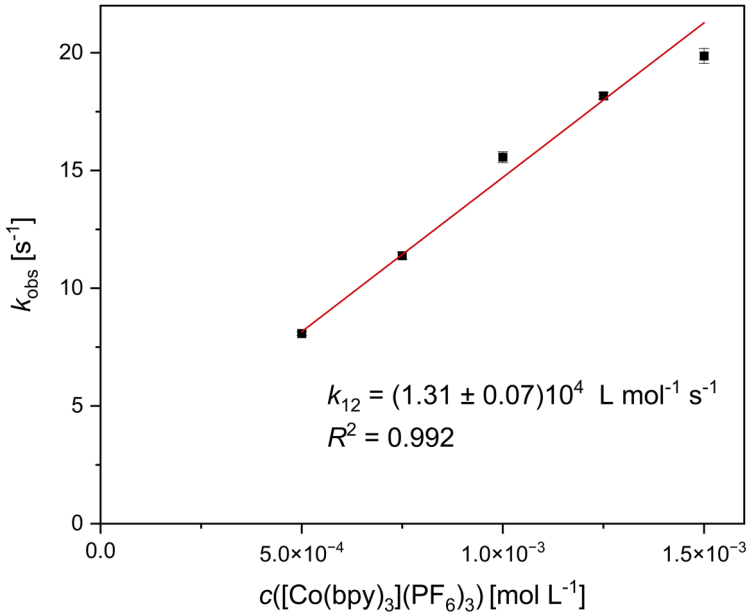


Figure S13: Plot of the reaction rate k_{obs} of the cross reaction between $[Cu(TMG2Phqu)_2]PF_6 \cdot CH_2Cl_2$ (**C1-PF$_6$**) and $[Co(bpy)_3](PF_6)_3$ against the concentration of $[Co(bpy)_3](PF_6)_3$. Some error bars are too small to be visualized properly.

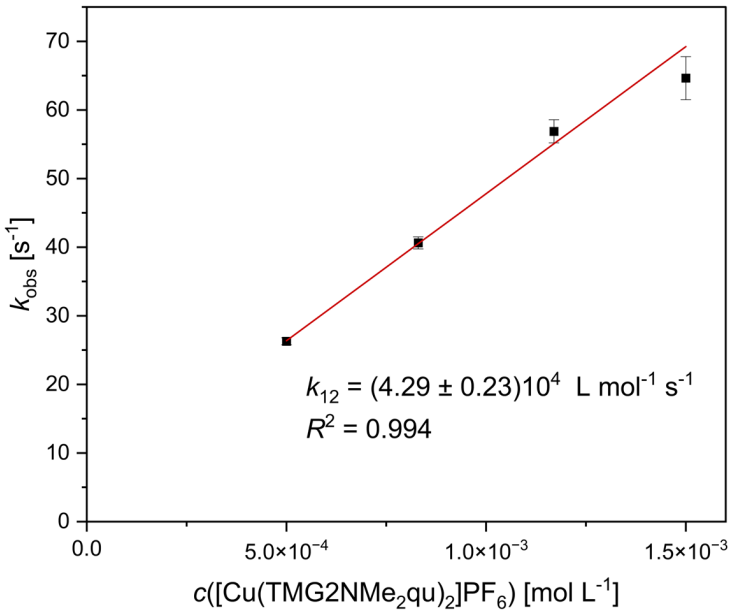


Figure S14: Plot of the reaction rate k_{obs} of the cross reaction between [Cu(TMG2Phqu)$_2$](OTf)$_2$·0.5 H_2O (**C2-OTf**) and [Cu(TMG2NMe$_2$qu)$_2$]PF_6·2 CH_2Cl_2 (**C3-PF$_6$**) against the concentration of **C3-PF$_6$**. Some error bars are too small to be visualized properly.

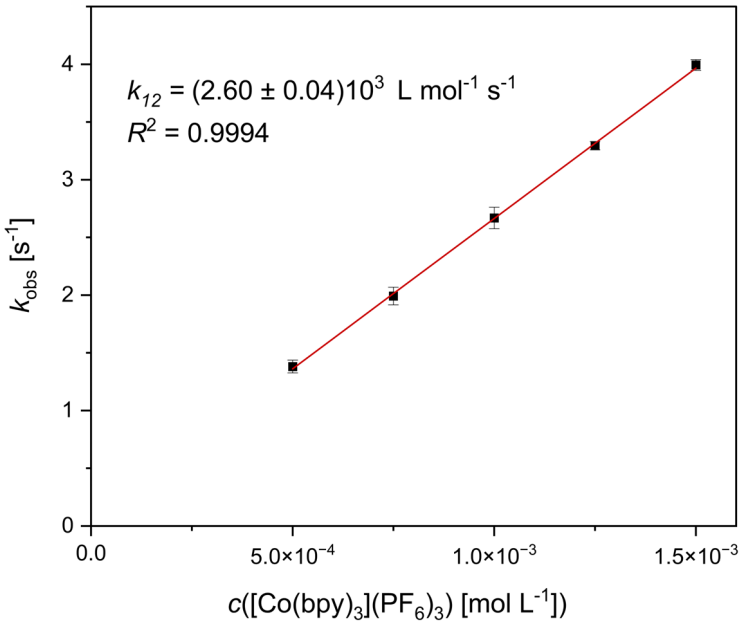


Figure S15: Plot of the reaction rate k_{obs} of the cross reaction between [Cu(TMG2NMe$_2$qu)$_2$]PF_6·2 CH_2Cl_2 (**C3-PF$_6$**) and [Co(bpy)$_3$](PF$_6$)$_3$ against the concentration of [Co(bpy)$_3$](PF$_6$)$_3$. Some error bars are too small to be visualized properly.

Table S6: Redox potentials $E_{1/2}$ differences between the redox potentials of the copper redox couple and the counter complex $\Delta E_{1/2}$, equilibrium constants K_{12}, reaction rates k_{12} and electron self-exchange rates k_{11}.

	$E_{1/2}$ [V] vs. Fc/Fc^+	$\Delta E_{1/2}$ [V]	K_{12} [ ]	k_{12} [L mol^{-1} s^{-1}]	k_{11} [L mol^{-1} s^{-1}]
C1-PF_6	-0.239	0.183	$1.23 \cdot 10^3$	$(1.31 \pm 0.07) \cdot 10^4$	$(1.15 \pm 0.12) \cdot 10^5$
C2-OTf	-0.220	0.115	$8.79 \cdot 10^1$	$(4.29 \pm 0.24) \cdot 10^4$	$(1.51 \pm 0.17) \cdot 10^5$
C3-PF_6	-0.335	0.279	$4.88 \cdot 10^6$	$(2.60 \pm 0.04) \cdot 10^3$	$(1.64 \pm 0.05) \cdot 10^2$

7 EPR Spectra

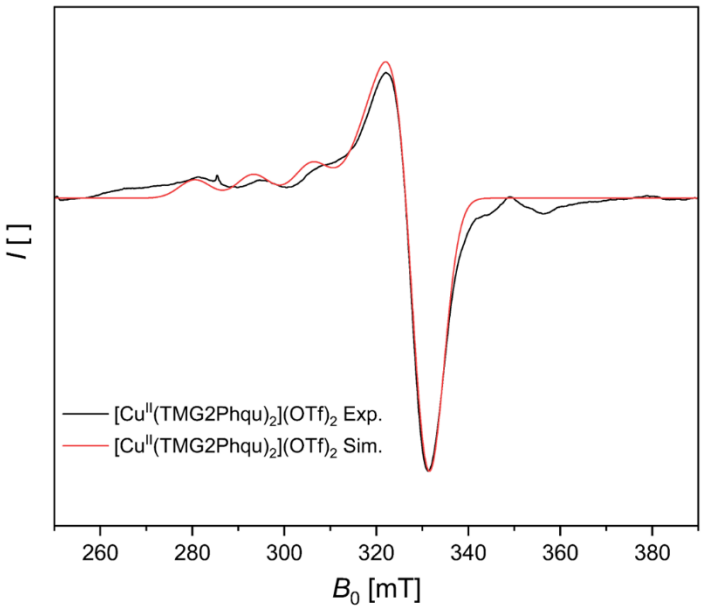


Figure S16: Experimental EPR spectrum of $[Cu(TMG2Phqu)_2](OTf)_2$ (**C2-OTf**) (c = 5 mM) in MeCN solution at 77 K (black) and simulated EPR spectrum (red).

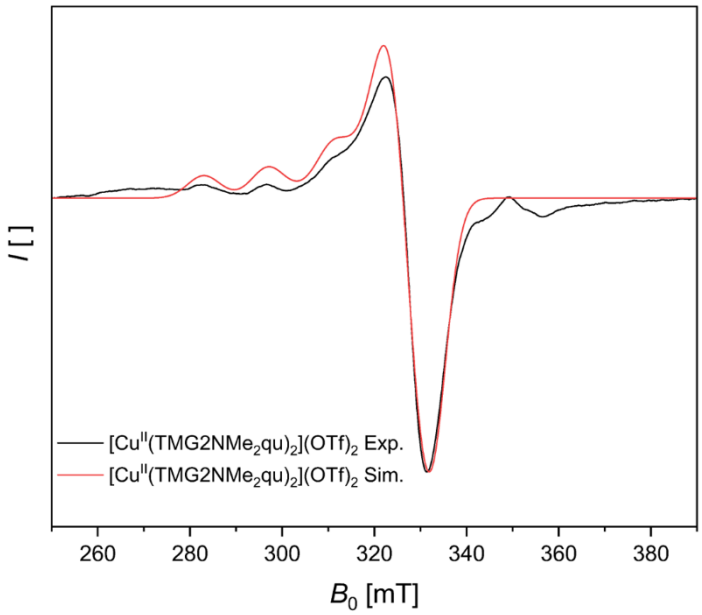


Figure S17: Experimental EPR spectrum of [Cu(TMG2NMe$_2$qu)$_2$](OTf)$_2$ (**C4-OTf**) (*c* = 5 mM) in MeCN solution at 77 K (black) and simulated EPR spectrum (red).

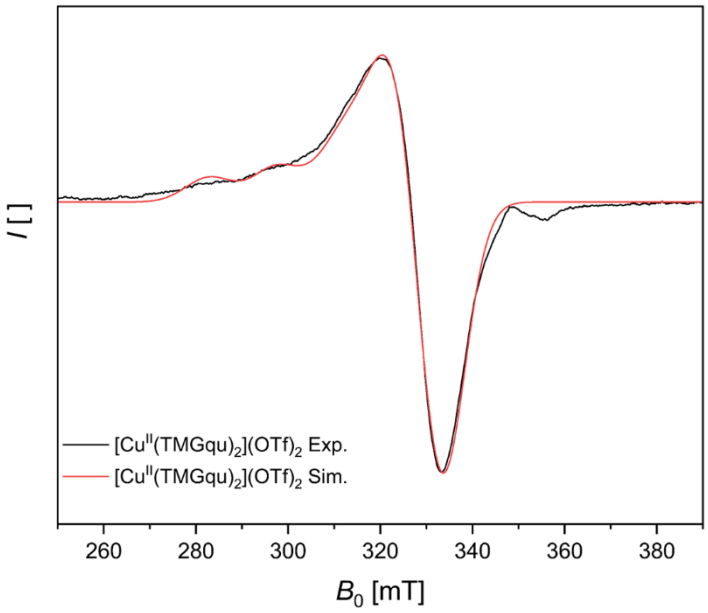


Figure S18: Experimental EPR spectrum of [Cu(TMGqu)$_2$](OTf)$_2$ (*c* = 5 mM) in MeCN solution at 77 K (black) and simulated EPR spectrum (red).

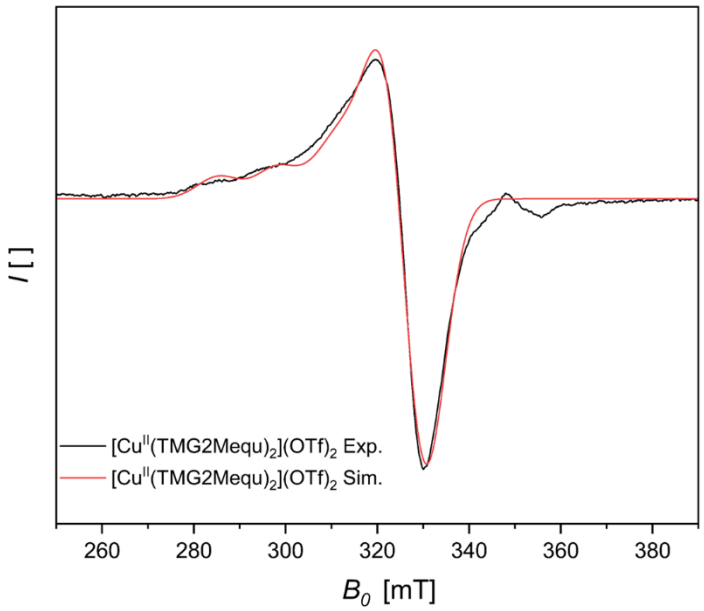


Figure S19: Experimental EPR spectrum of $[Cu(TMG2Mequ)_2](OTf)_2$ (c = 5 mM) in MeCN solution at 77 K (black) and simulated EPR spectrum (red).

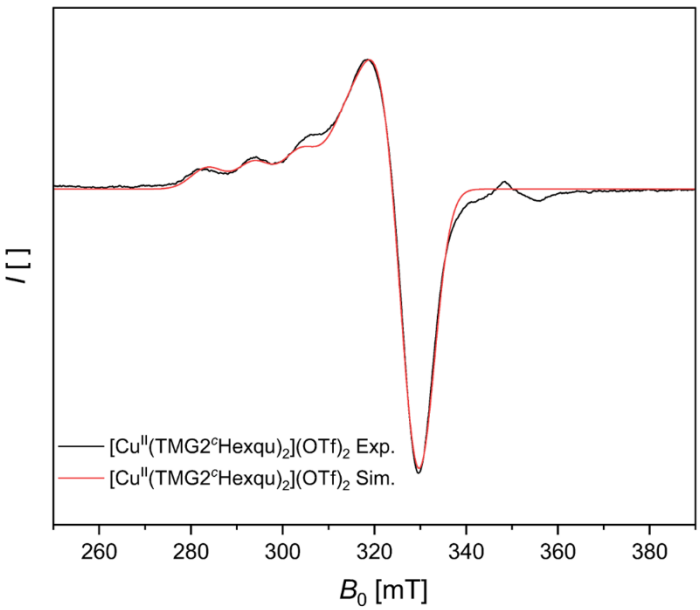


Figure S20: Experimental EPR spectrum of $[Cu(TMG2^cHexqu)_2](OTf)_2$ (c = 5 mM) in MeCN solution at 77 K (black) and simulated EPR spectrum (red).

Table S7: τ_4 values obtained by XRD and DFT as well as *g*-factors and *A*-values of the copper complexes listed measured in MeCN solution at 77 K. All spectra are axial.

	$\tau_{4,XRD}$	$\tau_{4,DFT}$	$g_\parallel$ [ ]	$g_\perp$ [ ]	$A_\parallel$ [G]	$A_\perp$ [G]
$[Cu(TMGqu)_2](OTf)_2$[a]	0.40	0.43	2.213	2.060	158	10
$[Cu(TMG2NMe_2qu)_2](OTf)_2$ (**C4-OTf**)	0.49	0.51	2.217	2.065	150	8
$[Cu(TMG2Mequ)_2](OTf)_2$[a]	0.49	0.52	2.214	2.071	138	0
$[Cu(TMG2Phqu)_2](OTf)_2$ (**C2-OTf**)	0.52	0.55	2.249	2.058	138	10
$[Cu(TMG2^cHexqu)_2](OTf)_2$[a]	0.63	0.65	2.256	2.068	111	19

a: Structural parameters taken from Herres-Pawlis et al.[1]

8 Marcus Theory

The Marcus theory describes the outer-sphere electron-transfer between two metal complexes.[19] If two metal complexes that only differ in charge (C_1 and C_1^+ or C_2 and C_2^+) are involved in such a reaction, it is called a self-exchange reaction, while a reaction between two different systems (e.g. C_1 and C_2^+) is referred to as a cross-reaction (see Scheme S1). In the case of reactions starting from **C1-PF$_6$** and **C3-PF$_6$**, complex C_1 corresponds to $[Cu^I(TMG2Phqu)_2]^+$ and $[Cu^I(TMG2NMe_2qu)_2]^+$, respectively, while complex C_2^+ corresponds to the counter complex $[Co(bpy)_3]^{3+}$. Strictly following this formalism, the self-exchange rate of **C2-OTf** would have been k_{22}, as it acts like C_2^+. This was ignored for the sake of simplicity.

$$C_1 + C_2^+ \xrightarrow{k_{12}} C_1^+ + C_2$$

$$C_2 + C_2^+ \xrightarrow{k_{22}} C_2^+ + C_2$$

$$C_1 + C_1^+ \xrightarrow{k_{11}} C_1^+ + C_1$$

Scheme S1: Schematic representations of the cross-reaction and the two self-exchange reaction that can occur between two redox couples.

Using the Marcus cross relation, which emerges from the Marcus theory, the cross-reaction rate (k_{12}) of an outer-sphere electron-transfer between two metal complexes can be utilized together with one self-exchange rate (e.g. k_{22}) to determine the remaining self-exchange rate (here: k_{11}):

$$k_{11} = \frac{{k_{12}}^2}{k_{22} \cdot K_{12} \cdot f_{12} \cdot {W_{12}}^2} \quad (1)$$

In this equation, K_{12} represents the equilibrium constant of the cross-reaction. It depends on the difference between the redox potentials $\Delta E_{1/2}$ of the involved complexes' redox couples (C_1/C_1^+ and C_2/C_2^+).

$$K_{12} = \exp\left(\frac{\Delta E_{1/2} \cdot \mathrm{n} \cdot \mathrm{F}}{\mathrm{R} \cdot T}\right) \quad (2)$$

W_{12} is the work term and describes the electrostatic work that occurs during the cross reaction (Equation 3). It includes the electrostatic work w_{ij} that must be overcome for the approach of two complex cations and is shown in Equation 5.

$$W_{12} = \exp\left(\frac{w_{11} + w_{22} - w_{12} - w_{21}}{2 \cdot \mathrm{R} \cdot T}\right) \quad (3)$$

f_{12} represents a correction term that adjusts the obtained rate constant to account for differences in reorganization energy and driving force between the self-exchange reactions and the cross-reaction.

$$f_{12} = \exp\left(\frac{\left(\ln K_{12} + \frac{w_{12} - w_{21}}{\mathrm{R} \cdot T}\right)^2}{4 \cdot \left(\ln\left(\frac{k_{22} \cdot k_{22}}{Z^2}\right) + \frac{w_{11} + w_{22}}{\mathrm{R} \cdot T}\right)}\right) \quad (4)$$

Z^2 represents the formation constant of the outer-sphere complex and is usually 10^{22} M^{-2} s^{-2}.[20]

The term w_{ij} must be considered for each possible permutation of the cation C_1, C_1^+, C_2 and C_2^+.

$$w_{ij} = \frac{Z_i \cdot Z_j \cdot e^2 \cdot N_A}{\varepsilon \cdot (a_i + a_j) \cdot (1 + \beta \cdot (a_i + a_j) \cdot \sqrt{\mu})} \quad (5)$$

$Z_{i/j}$ represents the cation's corresponding charge, $a_{i/j}$ is corresponding radius that has been determined for the employed complexes via the collision diameter of the geometry optimized DFT structures. ε is the permittivity of the solvent and μ is the ionic strength. The parameter β describes the Debye-Hückel constant and is described as follows:

$$\beta = \sqrt{\frac{8 \cdot \pi \cdot e^2 \cdot N_A}{1000 \cdot \varepsilon \cdot k_B \cdot T}} \quad (6)$$

The temperature T amounts to 298.15 K and $k_B = 1.38 \cdot 10^{-23}$. The constants and parameters used in this work are listed in Table S8.

Table S8: Used parameters and constants to determine the self-exchange rates of the studied complexes in this work.

Complex (C)		**C3-PF_6**	**C1-PF_6**	**C2-OTf**
Counter complex (CC)	-	$[Co(bpy)_3]^{3+}$	$[Co(bpy)_3]^{3+}$	$[Cu^{I}(TMG2NMe_2qu)_2]^{+}$
r(C)	[nm]	0.58	0.62	0.62
r(CC)	[nm]	0.70	0.70	0.58
$E_{1/2}$ (CC)	[V] vs Fc/Fc^+	-0.056	-0.056	-0.335
k_{22}	[L mol^{-1} s^{-1}]	0.645	0.645	164
β	[$m^{0.5}$ mol^{-1}]	$4.88 \cdot 10^{-6}$	$4.88 \cdot 10^{-6}$	$4.88 \cdot 10^{-6}$
w_{11}	[J mol^{-1}]	$6.63 \cdot 10^{3}$	$6.25 \cdot 10^{3}$	$6.25 \cdot 10^{3}$
w_{12}	[J mol^{-1}]	$9.03 \cdot 10^{3}$	$8.79 \cdot 10^{3}$	$6.43 \cdot 10^{3}$
w_{21}	[J mol^{-1}]	$1.20 \cdot 10^{4}$	$1.17 \cdot 10^{4}$	$6.43 \cdot 10^{3}$
w_{22}	[J mol^{-1}]	$1.65 \cdot 10^{4}$	$1.65 \cdot 10^{4}$	$6.63 \cdot 10^{3}$
W_{12}	[ ]	1.53	1.59	1.00
k_B	[J K^{-1}]	$1.38 \cdot 10^{-23}$	$1.38 \cdot 10^{-23}$	$1.38 \cdot 10^{-23}$
E_{MeCN}	[C V^{-1} m^{-1}]	$3.97 \cdot 10^{-9}$	$3.97 \cdot 10^{-9}$	$3.97 \cdot 10^{-9}$
μ	[mol m^{-3}]	1.60	1.60	1.60
f_{12}	-	0.531	0.747	0.839

9 Computational Details

9.1 General

Density functional theory (DFT) calculations were performed with Gaussian 16, Revision B.01 using the default UltraFine grid (a 99,590 grid).[21] The geometry optimizations of each conformer were started from the corresponding solid state structure and conducted using the TPSSh functional[22] and with the Ahlrichs type basis set def2-TZVP[23] as implemented in Gaussian 16, Revision B.01. As solvent model, the Polarizable Continuum Model (PCM) was used as

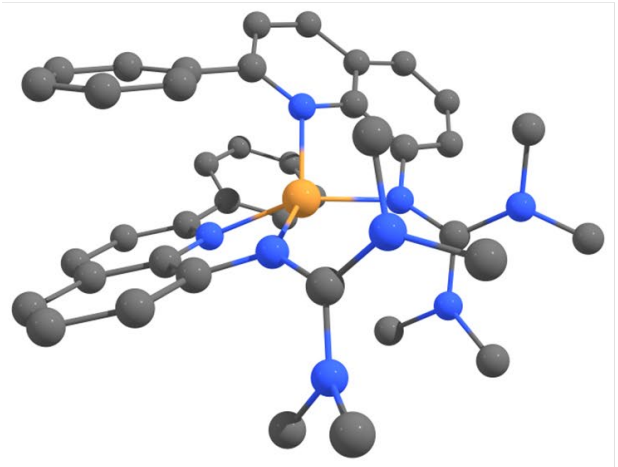
implemented in Gaussian 16. As empirical dispersion correction, the D3 dispersion with Becke–Johnson damping was used as implemented in Gaussian 16, Revision B.01.[24] Frequency calculations did not show imaginary values. For visualization and extraction of the calculated structural information Chemcraft (Version 1.8) was used. Calculated energy values were extracted directly from the output files using Notepad++ (Version 7.8.1).

To confirm the preferred conformer in solution, additional computations were carried out using the same basis set with MN15-L as functional.[25] For this, the structures were re-optimized from the solid state data as described above. The dispersion correction was omitted for these calculations. The xyz-coordinates of every optimized geometry as well as their single point energies are listed under section 11.

Conformer-rotamer ensemble sampling tool calculations

To verify the results of the DFT optimization calculations, conformer-rotamer ensemble sampling tool (CREST) calculations were performed.[26] The applied theory level was GFN2-xTB.[27] The minimum structures of the CREST calculations of **C1$_T$** and **C1$_C$** confirm the DFT results, the corresponding xyz-coordinates are listed under section 10 or can be accessed via RADAR4Chem.

Best Conformer starting from **C1$_C$**



Best Conformer starting from **C1$_T$**

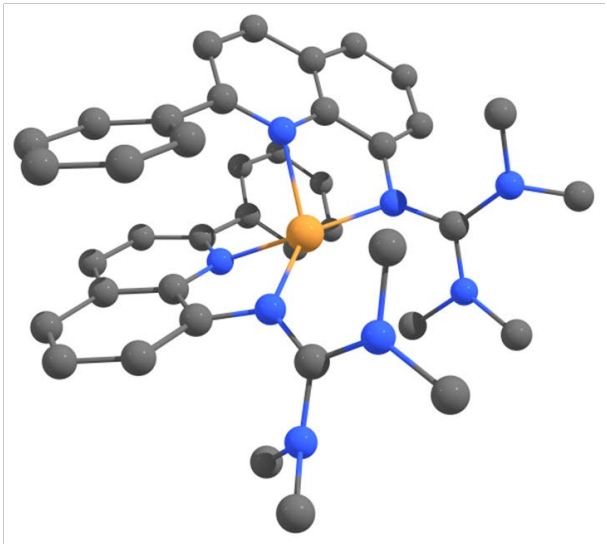


Figure S21: Depiction of the best conformers found via crest analysis starting from either conformer of the copper(I) complex. Hydrogen atoms were omitted for clarity.

9.2 Reorganization Energies

9.2.1 Theoretical Background

The total reorganization energy $\lambda_{11,T}$ of the whole electron self-exchange is divided in the internal reorganization energy $\lambda_{11,I}$ and the solvent reorganization energy $\lambda_{11,S}$ of the whole electron self-exchange (Equation 7).

$$\lambda_{11,T} = \lambda_{11,S} + \lambda_{11,I} \quad (7)$$

The total reorganization energy $\lambda_{11,T}$ and the internal reorganization energy $\lambda_{11,I}$ were calculated using DFT calculations and Nelsen's four-point method. The solvent reorganization energies $\lambda_{11,S}$ were obtained as the difference between the total and the internal reorganization energy.

The total reorganization energy ($\lambda_{Cu(I),T}$ for Cu(I) and $\lambda_{Cu(II),T}$ for Cu(II)) of each complex is calculated with its optimized ground state energy ($E_{Cu(I)L(I)S(I)}$ for Cu(I) and $E_{Cu(II)L(II)S(II)}$ for Cu(II)) and the energy of the complex with the same oxidation state but structure and solvent sphere of the complementary complex ($E_{Cu(I)L(II)S(II)}$ for Cu(I) and $E_{Cu(II)L(I)S(I)}$ for Cu(II), Equation 8). The indices Cu(I) or Cu(II) represent the oxidation state, L(I) or L(II) represent the ground state complex structure of the appropriate oxidation state and S(I) or S(II) represent the ground state solvent sphere of the appropriate oxidation state. In Fig. S22 (left) the energies $E_{Cu(I)}(x)$ and $E_{Cu(II)}(x)$ of the Cu(I) and Cu(II) complex are functions of the complex structure and the solvent sphere which are represented by the variable x_{LS}. The ground state complex structures and ground state solvent spheres for each oxidation state are represented by $x_{L(I)S(I)}$ and $x_{L(II)S(II)}$.

$$\lambda_{11,T} = \lambda_{Cu(II),T} + \lambda_{Cu(I),T} = (E_{Cu(II)L(I)S(I)} - E_{Cu(II)L(II)S(II)}) + (E_{Cu(I)L(II)S(II)} - E_{Cu(I)L(I)S(I)}) \quad (8)$$

The internal reorganization energy $\lambda_{11,I}$ for the whole electron self-exchange is the sum of the internal reorganization energies $\lambda_{Cu(I),I}$ and $\lambda_{Cu(II),I}$. λ_I of each complex is calculated with its optimized ground state energy ($E_{Cu(I)L(I)S(I)}$ for Cu(I) and $E_{Cu(II)L(II)S(II)}$ for Cu(II)) and the energy of the complex with the same oxidation state but with the structure of the complementary complex ($E_{Cu(I)L(II)S(I)}$ for Cu(I) and $E_{Cu(II)L(I)S(II)}$ for Cu(II)). In contrast to the total reorganization energy, the solvent sphere is allowed to relax for the calculated oxidation state.

$$\lambda_{11,I} = \lambda_{Cu(II),I} + \lambda_{Cu(I),I} = (E_{Cu(II)L(I)S(I_I)} - E_{Cu(II)L(II)S(II)}) + (E_{Cu(I)L(II)S(I)} - E_{Cu(I)L(I)S(I)}) \quad (9)$$

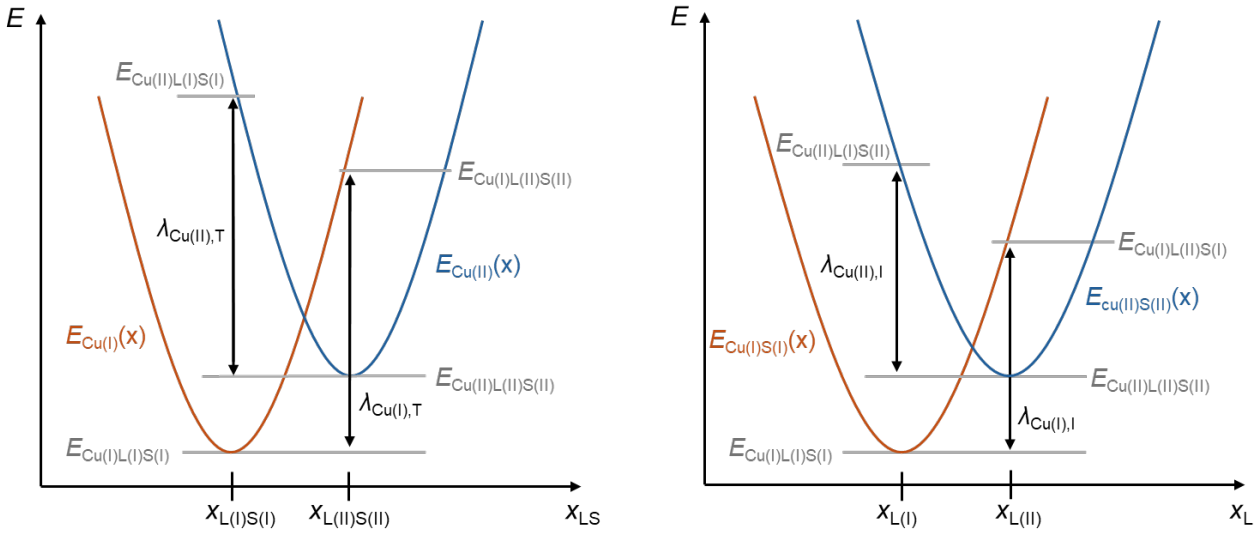


Figure S22: Schematic illustration of the Nelsen's four-point method for the calculation of the total reorganization energy $\lambda_{11,T}$ (left) and the internal reorganization energy $\lambda_{11,I}$ (right).

The keywords used in the computations of this procedure were chosen as described by Herres-Pawlis *et al.*[1] The reorganization energies obtained through this method are listed in Table S9.

Table S9: Inner, outer and total reorganization energies of **R1$_{cis}$** and **R2** using Nelsen's four-point method.

	$\lambda_{11,I}$ [kJ/mol]	$\lambda_{11,S}$ [kJ/mol]	$\lambda_{11,T}$ [kJ/mol]
$[Cu^{I}(TMG2Phqu)_2]^{+/2+}$: **R1$_{cis}$**	45.6	119.5	165.1
$[Cu^{I}(TMG2NMe_2qul)_2]^{+/2+}$: **R2**	68.4	-	-

9.2.2 Continuum Method

As an alternative approach to obtaining outer reorganization energies is the continuum method first described by Marcus and Sutin[19] and was used as described by Solomon, Fukuzumi and Karlin *et al.*[28] It describes the outer sphere reorganization as a function of molecular radii, distance and amount of transferred charge and the solvent's polarity as follows:

$$\lambda_{11,S,cont} = (\Delta e)^2 \cdot \left(\frac{1}{a_1} + \frac{1}{a_2} - \frac{1}{r}\right) \cdot \left(\frac{1}{D_{opt}} - \frac{1}{D_{Stat}}\right) \qquad (10)$$

where $\lambda_{11,s,cont}$ is the outer sphere reorganization energy, Δe is the change in charge upon the electron transfer ($(\Delta e)^2$ = 1.439976 MeV fm), a_1 and a_2 are the molecular radii in fm, r is the distance in fm, D_{opt} is the dynamic dielectric constant (frequently approximated as the square of

the refractive index), D_{stat} is the normal dielectric constant of the solvent. The radii were determined via the collision diameters of the Cu(I) and Cu(II) complexes participating in the self-exchange reaction.

10 Bibliography

[1] J. Heck, F. Metz, S. Buchenau, M. Teubner, B. Grimm-Lebsanft, T. P. Spaniol, A. Hoffmann, M. A. Rubhausen, S. Herres-Pawlis, *Chem. Sci.* **2022**, *13*, 8274-8288.

[2] A. J. Niestroj, M. E. Maier, *Angew. Chem.* **1997**, *109*, 1854-1854.

[3] a) H. Eilingsfeld, G. Neubauer, M. Seefelder, H. Weidincer, *Chem. Ber.* **1964**, *97*, 1232-1245; b) S. Herres-Pawlis, A. Neuba, O. Seewald, T. Seshadri, H. Egold, U. Flörke, G. Henkel, *Eur. J. Org. Chem.* **2005**, *2005*, 4879-4890.

[4] G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* **2010**, *29*, 2176-2179.

[5] a) P. Tremouilhac, C. L. Lin, P. C. Huang, Y. C. Huang, A. Nguyen, N. Jung, F. Bach, R. Ulrich, B. Neumair, A. Streit, S. Brase, *Angew. Chem. Int. Ed.* **2020**, *59*, 22771-22778; b) P. Tremouilhac, P. C. Huang, C. L. Lin, Y. C. Huang, A. Nguyen, N. Jung, F. Bach, S. Bräse, *Chemistry–Methods* **2020**, *1*, 8-11.

[6] *X-Area Pilatus3_SV 1.31. 170.0* **2020**, *STOE*.

[7] *X-Area Recipe 1.33.0.0* **2015**, *STOE*.

[8] *X-Area Integrate 1.71.0.0* **2016**, *STOE*.

[9] *X-Area LANA 1.83.8.0* **2020**, *STOE*.

[10] G. Sheldrick, *Acta Crystallogr. Sect. A* **2015**, *71*, 3-8.

[11] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112-122.

[12] G. M. Sheldrick, *Acta Crystallogr. Sect. C* **2015**, *71*, 3-8.

[13] C. B. Hübschle, G. M. Sheldrick, B. Dittrich, *J. Appl. Crystallogr.* **2011**, *44*, 1281-1284.

[14] a) A. Spek, P. A. M. C. Tool, **2008**, *65*; b) A. L. Spek, *Acta Crystallogr. Sect. D. Biol. Crystallogr.* **2009**, *65*, 148-155.

[15] S. Stoll, A. Schweiger, *J. Magn. Reson.* **2006**, *178*, 42-55.

[16] P. D. Nahide, C. Alba-Betancourt, R. Chávez-Rivera, P. Romo-Rodríguez, M. Solís-Hernández, L. A. Segura-Quezada, K. R. Torres-Carbajal, R. Gámez-Montaño, M. A. Deveze-Álvarez, M. A. Ramírez-Morales, *Bioorg. Med. Chem. Lett.* **2022**, *63*, 128649.

[17] W. Kantlehner, E. Haug, W. W. Mergen, P. Speh, T. Maier, J. J. Kapassakalidis, H. J. Bräuner, H. Hagen, *Liebigs Ann. Chem.* **1984**, *1984*, 108-126.

[18] L. Yang, D. R. Powell, R. P. Houser, *Dalton Trans.* **2007**, *9*, 955-964.

[19] R. A. Marcus, N. Sutin, *Biochim. Biophys. Acta* **1985**, *811*, 265-322.

[20] a) P. Comba, M. Kerscher, A. Roodt, *Eur. J. Inorg. Chem.* **2004**, *2004*, 4640-4645; b) M. J. Martin, J. F. Endicott, L. Ochrymowycz, D. Rorabacher, *Inorg. Chem.* **1987**, *26*, 3012-3022.

[21] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, M. C. X. Li, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S.Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, *Gaussian 16*, Gaussian Inc., Wallington CT, **2016**.

[22] a) V. Staroverov, G. Scuseria, J. Tao, J. Perdew, *J. Chem. Phys.* **2003**, *119*, 12129-12137; b) J. Tao, J. P. Perdew, V. N. Staroverov, G. E. Scuseria, *Phys. Rev. Lett.* **2003**, *91*, 146401.

[23] a) A. Schäfer, H. Horn, R. Ahlrichs, *J. Chem. Phys.* **1992**, *97*, 2571-2577; b) F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297-3305; c) K. Eichkorn, F. Weigend, O. Treutler, R. Ahlrichs, *Theor. Chem. Acc.* **1997**, *97*, 119-124.

[24] a) A. Hoffmann, R. Grunzke, S. Herres-Pawlis, *J. Comput. Chem.* **2014**, *35*, 1943-1950; b) L. Goerigk, S. Grimme, *Phys. Chem. Chem. Phys.* **2011**, *13*; c) S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456-1465.

[25] H. S. Yu, X. He, D. G. Truhlar, *J. Chem. Theory Comput.* **2016**, *12*, 1280-1293.

[26] P. Pracht, F. Bohle, S. Grimme, *Phys. Chem. Chem. Phys.* **2020**, *22*, 7169-7192.

[27] C. Bannwarth, S. Ehlert, S. Grimme, *J. Chem. Theory Comput.* **2019**, *15*, 1652-1671.

[28] R. Cao, C. Saracini, J. W. Ginsbach, M. T. Kieber-Emmons, M. A. Siegler, E. I. Solomon, S. Fukuzumi, K. D. Karlin, *J. Am. Chem. Soc.* **2016**, *138*, 7055-7066.

11 xyz-Coordinates of Optimized Structures, Electronic Energies and Thermal Corrections

11.1 Cu(I) Structures optimized with TPSSh

Trans conformer $C1_T$

Cu	-0.115387000	-0.047584000	-0.157083000
N	-2.039689000	0.255288000	-0.922483000
N	-0.580106000	1.641403000	0.861170000
C	3.041426000	-1.046718000	-2.761176000
H	3.366819000	-0.172813000	-3.313374000
N	-4.158177000	-0.821657000	-0.905525000
C	3.580679000	-2.305227000	-3.070446000
H	4.321495000	-2.379727000	-3.858306000
N	-2.410190000	-1.642828000	-2.186688000
C	3.179938000	-3.434176000	-2.392446000
H	3.595907000	-4.407457000	-2.624273000
N	1.458443000	0.301097000	-1.464539000
C	2.212045000	-3.325081000	-1.369796000
N	0.711953000	-1.892249000	-0.067115000
C	1.647839000	-2.058496000	-1.058278000
N	3.418961000	1.577786000	-1.105087000
C	1.767744000	-4.433768000	-0.612373000
H	2.148121000	-5.422919000	-0.840744000
N	1.472180000	2.574839000	-1.885359000
C	0.876302000	-4.242102000	0.405294000
H	0.530115000	-5.075435000	1.002077000
C	0.369519000	-2.946764000	0.677195000
C	-0.512050000	-2.755865000	1.846145000
C	-0.227859000	-3.450477000	3.029680000
H	0.620887000	-4.123164000	3.065845000
C	-0.993107000	-3.249852000	4.171754000

H	-0.745476000	-3.779936000	5.083822000
C	-2.064488000	-2.360593000	4.146713000
H	-2.661212000	-2.200424000	5.036921000
C	-2.365841000	-1.679170000	2.970812000
H	-3.204162000	-0.993928000	2.946796000
C	-1.597009000	-1.874271000	1.829133000
H	-1.828677000	-1.338536000	0.916985000
C	-2.472133000	1.532318000	-0.607416000
C	2.122034000	1.449837000	-1.498843000
C	4.335926000	2.523433000	-1.727528000
H	5.194050000	1.972706000	-2.124958000
H	4.699020000	3.260612000	-1.005937000
H	3.838032000	3.034369000	-2.547846000
C	4.027931000	0.620674000	-0.196051000
H	4.619182000	-0.127260000	-0.733998000
H	3.252176000	0.121837000	0.380325000
H	4.679510000	1.165554000	0.488517000
C	1.705483000	3.871750000	-1.263795000
H	2.415993000	3.765451000	-0.448121000
H	0.760586000	4.244859000	-0.859428000
H	2.086889000	4.598776000	-1.985763000
C	0.294348000	2.482731000	-2.733736000
H	0.316441000	3.305308000	-3.452648000
H	-0.626581000	2.549462000	-2.149527000
H	0.311043000	1.533934000	-3.262443000
C	-3.545802000	2.183059000	-1.203178000
H	-4.134824000	1.658932000	-1.945847000
C	-3.870647000	3.509293000	-0.874535000
H	-4.717487000	3.976310000	-1.364053000
C	-3.131711000	4.217187000	0.045779000
H	-3.382140000	5.239891000	0.301411000
C	-2.014818000	3.606228000	0.657022000
C	-1.675773000	2.265023000	0.330608000
C	-1.185043000	4.271350000	1.589861000
H	-1.416973000	5.291194000	1.875061000
C	-0.105904000	3.623055000	2.124652000
H	0.523978000	4.109860000	2.857054000
C	0.186338000	2.293007000	1.736910000
C	1.350663000	1.592808000	2.311604000
C	2.522234000	2.290738000	2.628060000
H	2.594317000	3.351016000	2.415940000
C	3.608963000	1.627347000	3.186136000
H	4.514885000	2.177449000	3.412007000
C	3.539690000	0.259839000	3.440995000
H	4.388260000	-0.255741000	3.875204000
C	2.375364000	-0.441316000	3.135224000
H	2.307133000	-1.503423000	3.339393000
C	1.289870000	0.220198000	2.575525000
H	0.376213000	-0.318885000	2.362889000
C	-2.870903000	-0.692899000	-1.334617000
C	-1.277550000	-1.366004000	-3.055576000
H	-0.359043000	-1.806559000	-2.660620000
H	-1.144050000	-0.291955000	-3.138911000
H	-1.478344000	-1.794303000	-4.040924000
C	-2.770904000	-3.049253000	-2.053645000
H	-3.280976000	-3.418407000	-2.947123000
H	-3.413169000	-3.184797000	-1.187063000
H	-1.857008000	-3.632192000	-1.906556000
C	-4.612843000	-0.267262000	0.357568000
H	-3.759077000	0.032305000	0.958101000
H	-5.181234000	-1.031971000	0.892867000
H	-5.252227000	0.606626000	0.199297000
C	-5.210987000	-1.369463000	-1.752898000
H	-4.821828000	-1.550192000	-2.751508000
H	-6.023721000	-0.639907000	-1.816146000
H	-5.610864000	-2.300829000	-1.342790000
C	2.082804000	-0.894705000	-1.766472000

E(RTPSSh) = -3630.31391282
Zero-point correction = 0.769575 (Hartree/Particle)
Thermal correction to Energy = 0.816740
Thermal correction to Enthalpy = 0.817684
Thermal correction to Gibbs Free Energy = 0.689090

Cis Conformer $C1_C$

N	0.388044000	1.721166000	1.210924000
C	0.665405000	1.820382000	2.506202000
N	1.673481000	1.068319000	3.007608000
C	2.672253000	0.527339000	2.095052000
H	2.263054000	-0.287516000	1.487260000
H	3.507009000	0.155401000	2.687906000
H	3.028641000	1.312996000	1.430719000
N	-0.031360000	2.610031000	3.378862000
C	1.704117000	0.565753000	4.375585000
H	0.802455000	0.865982000	4.899265000
H	2.575545000	0.947029000	4.913050000
H	1.754179000	-0.524800000	4.359450000
N	-1.030742000	1.312835000	-1.047288000
C	0.625995000	3.341454000	4.457740000
H	0.466680000	4.413714000	4.304892000
H	1.694712000	3.143821000	4.444109000
H	0.216167000	3.065242000	5.432796000
C	-1.388361000	3.044410000	3.090420000
H	-1.976675000	2.983908000	4.009355000
H	-1.830792000	2.397946000	2.337126000
H	-1.409894000	4.076346000	2.725702000
C	-0.008628000	2.837789000	0.486624000
C	0.362818000	4.143913000	0.783629000
H	0.967779000	4.336192000	1.661191000
C	0.000000000	5.217012000	-0.045672000
H	0.311697000	6.218199000	0.229044000
C	-0.720824000	5.011303000	-1.199630000
H	-0.992331000	5.835520000	-1.848606000
C	-1.086561000	3.697111000	-1.562310000
C	-0.741063000	2.606840000	-0.718986000
C	-1.764317000	3.392951000	-2.765599000
H	-2.057581000	4.198926000	-3.428772000
C	-2.025561000	2.089909000	-3.086655000
H	-2.542784000	1.836879000	-4.002667000
C	-1.634941000	1.051955000	-2.206647000
C	-1.876206000	-0.355485000	-2.574070000
C	-1.729229000	-0.773100000	-3.901820000
H	-1.430487000	-0.059531000	-4.660589000
C	-1.919007000	-2.106723000	-4.245449000
H	-1.777869000	-2.421747000	-5.272785000
C	-2.276221000	-3.036366000	-3.271901000
H	-2.420239000	-4.076608000	-3.539597000

C	-2.440505000	-2.625321000	-1.951468000
H	-2.714731000	-3.342983000	-1.187877000
C	-2.235606000	-1.296329000	-1.605282000
H	-2.347542000	-0.975989000	-0.578774000
Cu	0.000000000	0.000000000	0.123344000
N	-0.388044000	-1.721166000	1.210924000
C	-0.665405000	-1.820382000	2.506202000
N	-1.673481000	-1.068319000	3.007608000
C	-2.672253000	-0.527339000	2.095052000
H	-2.263054000	0.287516000	1.487260000
H	-3.507009000	-0.155401000	2.687906000
H	-3.028641000	-1.312996000	1.430719000
N	0.031360000	-2.610031000	3.378862000
C	-1.704117000	-0.565753000	4.375585000
H	-0.802455000	-0.865982000	4.899265000
H	-2.575545000	-0.947029000	4.913050000
H	-1.754179000	0.524800000	4.359450000
N	1.030742000	-1.312835000	-1.047288000
C	-0.625995000	-3.341454000	4.457740000
H	-0.466680000	-4.413714000	4.304892000
H	-1.694712000	-3.143821000	4.444109000
H	-0.216167000	-3.065242000	5.432796000
C	1.388361000	-3.044410000	3.090420000
H	1.976675000	-2.983908000	4.009355000
H	1.830792000	-2.397946000	2.337126000
H	1.409894000	-4.076346000	2.725702000
C	0.008628000	-2.837789000	0.486624000
C	-0.362818000	-4.143913000	0.783629000
H	-0.967779000	-4.336192000	1.661191000
C	0.000000000	-5.217012000	-0.045672000
H	-0.311697000	-6.218199000	0.229044000
C	0.720824000	-5.011303000	-1.199630000
H	0.992331000	-5.835520000	-1.848606000
C	1.086561000	-3.697111000	-1.562310000
C	0.741063000	-2.606840000	-0.718986000
C	1.764317000	-3.392951000	-2.765599000
H	2.057581000	-4.198926000	-3.428772000
C	2.025561000	-2.089909000	-3.086655000
H	2.542784000	-1.836879000	-4.002667000
C	1.634941000	-1.051955000	-2.206647000
C	1.876206000	0.355485000	-2.574070000
C	1.729229000	0.773100000	-3.901820000
H	1.430487000	0.059531000	-4.660589000
C	1.919007000	2.106723000	-4.245449000
H	1.777869000	2.421747000	-5.272785000
C	2.276221000	3.036366000	-3.271901000
H	2.420239000	4.076608000	-3.539597000
C	2.440505000	2.625321000	-1.951468000
H	2.714731000	3.342983000	-1.187877000
C	2.235606000	1.296329000	-1.605282000
H	2.347542000	0.975989000	-0.578774000

E(UTPSSh) = -3630.31643329
Zero-point correction = 0.770638 (Hartree/Particle)
Thermal correction to Energy = 0.817093
Thermal correction to Enthalpy = 0.818037
Thermal correction to Gibbs Free Energy = 0.693915

C3*

***The Structure was optimized from the solid state with frozen Cu–N bond lengths as TPPSSh was unable properly to simulate the observed lengthened bond lenghts.**

Cu	0.001044000	0.004042000	-0.035303000
N	-1.811317000	-0.500230000	-0.698659000
N	-0.088112000	-2.007665000	0.756198000
N	-4.064629000	0.204813000	-0.435326000
N	-2.534607000	1.492767000	-1.614971000
N	1.832218000	-2.063589000	2.085721000
N	1.810454000	0.500234000	-0.700891000
N	0.088768000	2.007947000	0.752839000
N	2.530334000	-1.493486000	-1.618371000
N	4.062519000	-0.209086000	-0.437590000
N	-1.832242000	2.064894000	2.081718000
C	-2.025307000	-1.874759000	-0.660955000
C	-3.020711000	-2.529690000	-1.376796000
H	-3.725720000	-1.942150000	-1.952708000
C	-3.113849000	-3.930411000	-1.398237000
H	-3.907529000	-4.397522000	-1.969780000
C	-2.194968000	-4.702036000	-0.724426000
H	-2.242461000	-5.784812000	-0.749349000
C	-1.156402000	-4.075428000	-0.001912000
C	-1.071862000	-2.661020000	0.060421000
C	-0.143748000	-4.802239000	0.672006000
H	-0.164971000	-5.886301000	0.650698000
C	0.845016000	-4.149990000	1.344200000
H	1.602608000	-4.713424000	1.867322000
C	0.848590000	-2.720649000	1.389455000
C	-2.795864000	0.361576000	-0.910975000
C	-4.348541000	-0.624895000	0.721455000
H	-3.425641000	-0.843186000	1.250317000
H	-4.818825000	-1.569118000	0.428000000
H	-5.026429000	-0.082561000	1.385987000
C	-5.235182000	0.673610000	-1.165632000
H	-4.930656000	1.079021000	-2.127149000
H	-5.777695000	1.439080000	-0.603634000
H	-5.907459000	-0.173027000	-1.336745000
C	-1.384861000	1.541657000	-2.505023000
H	-1.202940000	0.551809000	-2.915902000
H	-0.483028000	1.876512000	-1.981870000
H	-1.608419000	2.238801000	-3.315141000
C	-3.127070000	2.780171000	-1.273173000
H	-3.733518000	3.170604000	-2.094641000
H	-2.327630000	3.493864000	-1.058324000
H	-3.745766000	2.674081000	-0.385916000
C	1.554505000	-0.759626000	2.673848000
H	2.489064000	-0.346682000	3.048237000
H	0.848001000	-0.844340000	3.508089000
H	1.142266000	-0.077664000	1.929960000
C	2.866744000	-2.835444000	2.761852000
H	3.641276000	-2.143329000	3.087619000
H	3.320488000	-3.550799000	2.076371000
H	2.487767000	-3.373607000	3.640098000
C	2.027058000	1.874438000	-0.662370000
C	3.024026000	2.528605000	-1.376672000
H	3.728985000	1.940725000	-1.952291000
C	3.118707000	3.929265000	-1.396812000

H	3.913489000	4.395959000	-1.967160000
C	2.200051000	4.701461000	-0.723306000
H	2.248850000	5.784194000	-0.747406000
C	1.160020000	4.075545000	-0.002271000
C	1.074005000	2.661294000	0.058734000
C	0.147289000	4.802738000	0.671120000
H	0.169392000	5.886795000	0.650684000
C	-0.842650000	4.150747000	1.341864000
H	-1.600167000	4.714473000	1.864769000
C	-0.847635000	2.721414000	1.386294000
C	2.793564000	-0.363290000	-0.913564000
C	1.379656000	-1.539614000	-2.507394000
H	1.201909000	-0.550115000	-2.920992000
H	0.476701000	-1.868813000	-1.982581000
H	1.599541000	-2.239971000	-3.315695000
C	3.119872000	-2.782322000	-1.276663000
H	3.738311000	-2.677830000	-0.389015000
H	3.725939000	-3.173756000	-2.097924000
H	2.318829000	-3.494361000	-1.062411000
C	5.232295000	-0.680148000	-1.167693000
H	4.927239000	-1.083859000	-2.129763000
H	5.772596000	-1.447532000	-0.606169000
H	5.906769000	0.164965000	-1.337617000
C	4.347749000	0.619257000	0.719827000
H	3.425166000	0.838861000	1.248702000
H	4.819832000	1.562831000	0.427168000
H	5.024511000	0.075195000	1.384095000
C	-2.866886000	2.837528000	2.756825000
H	-3.642510000	2.146014000	3.081289000
H	-3.319044000	3.553606000	2.071065000
H	-2.488502000	3.374944000	3.635786000
C	-1.555494000	0.761359000	2.671425000
H	-2.490643000	0.349063000	3.045047000
H	-0.850111000	0.846845000	3.506531000
H	-1.142553000	0.078465000	1.928785000

E(RTPSSh) = -3436.04846909
Zero-point correction = 0.754272 (Hartree/Particle)
Thermal correction to Energy = 0.800389
Thermal correction to Enthalpy = 0.801333
Thermal correction to Gibbs Free Energy = 0.677397

11.2 Cu(II) Structures optimized with TPSSh

Trans Conformer $C2_T$

Cu	-0.082362000	0.050548000	-0.101823000
N	-1.741062000	0.905636000	-0.919160000
N	0.176885000	1.857054000	0.629497000
C	2.312162000	-2.243400000	-2.570272000
H	3.044086000	-1.626881000	-3.076401000
N	-4.101259000	0.705136000	-0.912256000
C	2.172603000	-3.592797000	-2.939987000
H	2.805151000	-3.983607000	-3.727714000
N	-2.776049000	-0.842309000	-2.025156000
C	1.266733000	-4.415689000	-2.312478000
H	1.178741000	-5.462096000	-2.576483000
N	1.554320000	-0.361140000	-1.164643000
C	0.443519000	-3.889588000	-1.293088000
N	-0.251804000	-1.938894000	0.000149000
C	0.544820000	-2.516500000	-0.954355000
N	3.893768000	-0.175760000	-0.972249000
C	-0.480173000	-4.661367000	-0.555088000
H	-0.611088000	-5.710197000	-0.793936000
N	2.611060000	1.649815000	-1.631211000
C	-1.179084000	-4.088039000	0.471807000
H	-1.865680000	-4.673535000	1.066684000
C	-1.044433000	-2.707012000	0.752884000
C	-1.716041000	-2.143656000	1.939743000
C	-1.778357000	-2.926035000	3.101097000
H	-1.361916000	-3.925664000	3.101220000
C	-2.327445000	-2.413420000	4.269438000
H	-2.351568000	-3.026382000	5.162178000
C	-2.832166000	-1.116356000	4.296666000
H	-3.258485000	-0.716301000	5.208547000
C	-2.786571000	-0.335976000	3.145156000
H	-3.184580000	0.671140000	3.156987000
C	-2.232545000	-0.846910000	1.978750000
H	-2.213729000	-0.237640000	1.086133000
C	-1.675571000	2.292111000	-0.792164000
C	2.688945000	0.356878000	-1.265339000
C	5.119221000	0.204593000	-1.670963000
H	5.592356000	-0.707636000	-2.041697000
H	5.816482000	0.715273000	-1.003524000
H	4.881179000	0.844043000	-2.516359000
C	4.025554000	-1.305781000	-0.061012000
H	4.206198000	-2.232501000	-0.611721000
H	3.122710000	-1.404290000	0.534957000
H	4.870401000	-1.111649000	0.600840000
C	3.575022000	2.658014000	-1.203610000
H	4.178482000	2.266654000	-0.389513000
H	3.019711000	3.528265000	-0.850007000
H	4.224493000	2.970484000	-2.024254000
C	1.551620000	2.130341000	-2.512367000
H	1.997465000	2.505669000	-3.437077000
H	1.004462000	2.942901000	-2.034295000
H	0.872861000	1.314185000	-2.737631000
C	-2.458645000	3.219477000	-1.462560000
H	-3.229808000	2.883025000	-2.143029000
C	-2.253351000	4.599688000	-1.283219000
H	-2.886233000	5.290739000	-1.826606000
C	-1.280521000	5.082022000	-0.437383000
H	-1.141800000	6.145603000	-0.289490000
C	-0.443344000	4.171659000	0.243149000
C	-0.636347000	2.781789000	0.044705000
C	0.596080000	4.551769000	1.123082000
H	0.770339000	5.604025000	1.314691000
C	1.363967000	3.598051000	1.739584000
H	2.135216000	3.876615000	2.444225000
C	1.141694000	2.228540000	1.471942000
C	1.924159000	1.172068000	2.129344000
C	3.281990000	1.348411000	2.420703000
H	3.784450000	2.263489000	2.131797000
C	3.994002000	0.344572000	3.064160000
H	5.047287000	0.485275000	3.273689000
C	3.361409000	-0.841894000	3.431479000
H	3.921343000	-1.620632000	3.934881000
C	2.008971000	-1.022058000	3.155852000
H	1.504009000	-1.932402000	3.454881000
C	1.294206000	-0.019486000	2.513291000
H	0.224797000	-0.131668000	2.372316000
C	-2.875512000	0.284196000	-1.290903000
C	-1.720835000	-1.015490000	-3.017250000
H	-1.158703000	-1.927383000	-2.816455000
H	-1.053504000	-0.159849000	-2.987924000
H	-2.171515000	-1.095191000	-4.010047000
C	-3.706822000	-1.958126000	-1.886622000
H	-4.373912000	-2.043953000	-2.747262000
H	-4.290792000	-1.834743000	-0.978253000
H	-3.120987000	-2.875726000	-1.807208000
C	-4.329908000	1.499333000	0.288533000
H	-3.419593000	1.567902000	0.874822000
H	-5.109026000	1.016226000	0.881479000
H	-4.654951000	2.507745000	0.022137000
C	-5.289323000	0.494605000	-1.738611000
H	-4.993745000	0.162793000	-2.730004000
H	-5.810706000	1.450149000	-1.825194000
H	-5.966086000	-0.234480000	-1.288286000
C	1.522594000	-1.691946000	-1.573097000

Zero-point correction = 0.773657 (Hartree/Particle)
Thermal correction to Energy = 0.819718
Thermal correction to Enthalpy = 0.820662
Thermal correction to Gibbs Free Energy = 0.695776

Cis Conformer $C2_C$

N	0.000000000	1.712848000	1.187919000
C	0.170581000	1.932377000	2.511527000
N	1.307877000	1.510868000	3.089757000
C	2.533453000	1.383829000	2.304808000
H	2.696023000	0.357608000	1.970953000
H	3.370532000	1.683442000	2.936304000
H	2.478420000	2.044409000	1.445780000
N	-0.768641000	2.553480000	3.255921000
C	1.425192000	1.143355000	4.497598000
H	0.441247000	1.080259000	4.950460000
H	2.031965000	1.867387000	5.044908000
H	1.912444000	0.168660000	4.558951000
N	-1.108319000	1.048248000	-1.134874000
C	-0.442348000	3.415450000	4.391903000
H	-0.934591000	4.377854000	4.234219000
H	0.630921000	3.575639000	4.440608000
H	-0.798223000	2.989755000	5.332136000
C	-2.165904000	2.596976000	2.839787000
H	-2.791721000	2.368497000	3.704373000
H	-2.340029000	1.862344000	2.059354000
H	-2.425315000	3.589338000	2.463146000
C	-0.489553000	2.752440000	0.391558000
C	-0.371603000	4.105594000	0.671806000
H	0.086739000	4.428198000	1.597877000
C	-0.808688000	5.075400000	-0.248285000
H	-0.691098000	6.121297000	0.008261000
C	-1.369085000	4.723163000	-1.454540000
H	-1.710664000	5.473883000	-2.156254000
C	-1.495543000	3.356524000	-1.783861000
C	-1.048156000	2.380383000	-0.859178000
C	-2.042027000	2.883148000	-2.997380000
H	-2.398407000	3.595232000	-3.732461000
C	-2.128067000	1.536347000	-3.234113000
H	-2.573752000	1.156286000	-4.143332000
C	-1.646019000	0.617226000	-2.276456000
C	-1.750572000	-0.833585000	-2.496210000
C	-1.456461000	-1.399842000	-3.740578000
H	-1.130066000	-0.768332000	-4.558301000
C	-1.541764000	-2.775283000	-3.915917000
H	-1.284309000	-3.210332000	-4.873996000
C	-1.944477000	-3.594244000	-2.863277000
H	-2.008067000	-4.666309000	-3.004339000
C	-2.266943000	-3.033130000	-1.630823000
H	-2.594408000	-3.664897000	-0.814488000
C	-2.165989000	-1.660590000	-1.448277000
H	-2.433655000	-1.209222000	-0.502275000
Cu	0.000000000	0.000000000	0.157689000
N	0.000000000	-1.712848000	1.187919000
C	-0.170581000	-1.932377000	2.511527000
N	-1.307877000	-1.510868000	3.089757000
C	-2.533453000	-1.383829000	2.304808000
H	-2.696023000	-0.357608000	1.970953000
H	-3.370532000	-1.683442000	2.936304000
H	-2.478420000	-2.044409000	1.445780000
N	0.768641000	-2.553480000	3.255921000
C	-1.425192000	-1.143355000	4.497598000
H	-0.441247000	-1.080259000	4.950460000
H	-2.031965000	-1.867387000	5.044908000
H	-1.912444000	-0.168660000	4.558951000
N	1.108319000	-1.048248000	-1.134874000
C	0.442348000	-3.415450000	4.391903000
H	0.934591000	-4.377854000	4.234219000
H	-0.630921000	-3.575639000	4.440608000
H	0.798223000	-2.989755000	5.332136000
C	2.165904000	-2.596976000	2.839787000
H	2.791721000	-2.368497000	3.704373000
H	2.340029000	-1.862344000	2.059354000
H	2.425315000	-3.589338000	2.463146000
C	0.489553000	-2.752440000	0.391558000
C	0.371603000	-4.105594000	0.671806000
H	-0.086739000	-4.428198000	1.597877000
C	0.808688000	-5.075400000	-0.248285000
H	0.691098000	-6.121297000	0.008261000
C	1.369085000	-4.723163000	-1.454540000
H	1.710664000	-5.473883000	-2.156254000
C	1.495543000	-3.356524000	-1.783861000
C	1.048156000	-2.380383000	-0.859178000
C	2.042027000	-2.883148000	-2.997380000
H	2.398407000	-3.595232000	-3.732461000
C	2.128067000	-1.536347000	-3.234113000
H	2.573752000	-1.156286000	-4.143332000
C	1.646019000	-0.617226000	-2.276456000
C	1.750572000	0.833585000	-2.496210000
C	1.456461000	1.399842000	-3.740578000
H	1.130066000	0.768332000	-4.558301000
C	1.541764000	2.775283000	-3.915917000
H	1.284309000	3.210332000	-4.873996000
C	1.944477000	3.594244000	-2.863277000
H	2.008067000	4.666309000	-3.004339000
C	2.266943000	3.033130000	-1.630823000
H	2.594408000	3.664897000	-0.814488000
C	2.165989000	1.660590000	-1.448277000
H	2.433655000	1.209222000	-0.502275000

E(UTPSSh) = -3630.15497357
Zero-point correction = 0.774351 (Hartree/Particle)
Thermal correction to Energy = 0.820118
Thermal correction to Enthalpy = 0.821063
Thermal correction to Gibbs Free Energy = 0.698153

C4

Cu	0.000001000	-0.000004000	0.108460000
C	2.748179000	0.672790000	-0.816986000
N	1.495368000	1.089257000	-0.558775000
C	1.910228000	-0.914341000	-2.479586000
H	1.210351000	-0.107599000	-2.675221000
H	2.416146000	-1.190730000	-3.406901000
H	1.372023000	-1.786446000	-2.102230000
N	2.914196000	-0.461480000	-1.522427000
C	4.056194000	-1.351133000	-1.342740000
H	3.680507000	-2.368999000	-1.225783000
H	4.726527000	-1.323582000	-2.204425000
H	4.602519000	-1.069542000	-0.447056000
N	3.839217000	1.342148000	-0.386004000
N	-0.769000000	1.778209000	0.656859000
C	5.085835000	1.392040000	-1.147137000
H	5.368812000	2.440963000	-1.262731000
H	5.892046000	0.867767000	-0.630015000
H	4.935153000	0.958440000	-2.131826000
C	3.800797000	2.203027000	0.788265000
H	2.870083000	2.054107000	1.325646000
H	4.641920000	1.945794000	1.435442000
H	3.882261000	3.253930000	0.499470000
C	1.147535000	2.442456000	-0.606324000
C	1.837763000	3.428777000	-1.298566000
H	2.757557000	3.180593000	-1.811748000
C	1.345828000	4.741424000	-1.373976000
H	1.914269000	5.481902000	-1.923288000
C	0.156005000	5.084960000	-0.773586000
H	-0.230894000	6.095268000	-0.828613000
C	-1.829673000	4.354425000	0.538521000
H	-2.250182000	5.352598000	0.498477000
C	-0.085511000	2.781998000	0.009260000
C	-0.581742000	4.101693000	-0.082298000
C	-1.926997000	2.054240000	1.279589000
C	-2.488466000	3.364539000	1.202434000
H	-3.417372000	3.579482000	1.706701000
C	-2.748263000	-0.672740000	-0.816770000
N	-1.495428000	-1.089222000	-0.558709000
C	-1.910472000	0.914554000	-2.479297000
H	-1.372269000	1.786653000	-2.101924000
H	-1.210582000	0.107849000	-2.675038000
H	-2.416469000	1.190987000	-3.406557000
N	-2.914349000	0.461596000	-1.522090000
C	-4.056338000	1.351222000	-1.342217000
H	-4.726747000	1.323748000	-2.203845000
H	-4.602581000	1.069542000	-0.446511000
H	-3.680647000	2.369081000	-1.225197000
N	0.769062000	-1.778254000	0.656647000
N	-3.839263000	-1.342143000	-0.385759000
C	-3.800743000	-2.203130000	0.788427000
H	-4.641796000	-1.945941000	1.435714000
H	-3.882258000	-3.254004000	0.499542000
H	-2.869973000	-2.054280000	1.325728000
C	-5.085939000	-1.391970000	-1.146801000
H	-5.892114000	-0.867746000	-0.629572000
H	-4.935333000	-0.958282000	-2.131462000
H	-5.368922000	-2.440884000	-1.262467000
C	-1.147586000	-2.442414000	-0.606408000
C	-1.837871000	-3.428685000	-1.298664000
H	-2.757721000	-3.180469000	-1.811732000
C	-1.345928000	-4.741320000	-1.374233000
H	-1.914416000	-5.481759000	-1.923551000
C	-0.156042000	-5.084894000	-0.773989000
H	0.230862000	-6.095193000	-0.829141000
C	0.581761000	-4.101677000	-0.082689000
C	0.085523000	-2.781997000	0.009028000
C	1.829754000	-4.354447000	0.537989000
H	2.250271000	-5.352612000	0.497821000
C	2.488601000	-3.364609000	1.201922000
H	3.417558000	-3.579582000	1.706082000
C	1.927123000	-2.054324000	1.279242000
N	-2.553613000	1.074535000	1.995023000
N	2.553787000	-1.074670000	1.994704000
C	-3.853512000	1.358937000	2.602516000
H	-4.288453000	0.413237000	2.918593000
H	-3.769050000	2.016832000	3.474627000
H	-4.522396000	1.812303000	1.873248000
C	-1.748479000	0.089488000	2.719839000
H	-1.097521000	0.582944000	3.447433000
H	-2.423968000	-0.578766000	3.247808000
H	-1.140961000	-0.513627000	2.047023000
C	3.853758000	-1.359093000	2.602035000
H	4.288705000	-0.413409000	2.918156000
H	3.769408000	-2.017073000	3.474091000
H	4.522578000	-1.812368000	1.872651000
C	1.748692000	-0.089717000	2.719695000
H	1.097783000	-0.583270000	3.447267000
H	2.424210000	0.578473000	3.247706000
H	1.141127000	0.513479000	2.046994000

E(UTPSSh) = -3435.89337528
Zero-point correction = 0.758899 (Hartree/Particle)
Thermal correction to Energy = 0.803925
Thermal correction to Enthalpy = 0.804869
Thermal correction to Gibbs Free Energy = 0.684519

11.3 Structures optimized with MN15-L

Cu(I) Trans conformer $C1_T$

Cu	-0.133494000	-0.088693000	-0.218633000
N	-2.107886000	-0.127353000	-0.966696000
N	-0.921264000	1.582224000	0.735153000
C	3.208770000	-0.630321000	-2.815167000
H	3.358042000	0.277539000	-3.411112000
N	-3.892278000	-1.700251000	-0.759011000
C	4.001122000	-1.775042000	-3.055946000
H	4.757465000	-1.741599000	-3.846068000
N	-2.071274000	-2.128737000	-2.138128000
C	3.829371000	-2.926789000	-2.306717000
H	4.441180000	-3.817935000	-2.477186000
N	1.354076000	0.436828000	-1.601654000
C	2.852011000	-2.954818000	-1.275916000
N	1.079854000	-1.762855000	-0.037617000
C	2.030180000	-1.809232000	-1.037395000
N	3.011096000	2.082068000	-1.134596000
C	2.666604000	-4.077628000	-0.423089000
H	3.259257000	-4.983044000	-0.592651000
N	0.949339000	2.672383000	-2.054478000
C	1.769947000	-3.993135000	0.617711000
H	1.622242000	-4.824890000	1.311422000
C	0.991890000	-2.812649000	0.794699000
C	0.103873000	-2.714760000	1.985206000
C	0.644177000	-3.028793000	3.246938000
H	1.682381000	-3.372676000	3.313566000
C	-0.110575000	-2.849134000	4.410759000
H	0.333951000	-3.067457000	5.386070000
C	-1.429053000	-2.385123000	4.323522000
H	-2.023953000	-2.244711000	5.230548000
C	-1.992316000	-2.117931000	3.068175000
H	-3.033383000	-1.790640000	3.004766000
C	-1.230002000	-2.275794000	1.904244000
H	-1.664839000	-2.078827000	0.919740000
C	-2.807908000	1.031806000	-0.654672000
C	1.788271000	1.694263000	-1.602999000
C	3.718063000	3.257472000	-1.632334000
H	4.734618000	2.953596000	-1.941722000
H	3.811585000	4.031439000	-0.846448000
H	3.195463000	3.681288000	-2.499991000
C	3.780106000	1.252125000	-0.215869000
H	4.511405000	0.614170000	-0.748249000
H	3.102455000	0.617474000	0.379296000
H	4.328121000	1.921458000	0.466434000
C	0.795810000	3.954175000	-1.370978000
H	1.420119000	3.982699000	-0.465251000
H	-0.262833000	4.069957000	-1.069040000
H	1.066486000	4.801287000	-2.026860000
C	-0.148649000	2.316735000	-2.945695000
H	-0.403141000	3.205455000	-3.546939000
H	-1.048081000	1.995736000	-2.386983000
H	0.161721000	1.500931000	-3.613871000
C	-4.038434000	1.405947000	-1.201677000
H	-4.549789000	0.714684000	-1.880558000
C	-4.622447000	2.659395000	-0.908758000
H	-5.585513000	2.912373000	-1.362458000
C	-3.991041000	3.563863000	-0.071763000
H	-4.434361000	4.537425000	0.158508000
C	-2.734993000	3.228651000	0.500164000
C	-2.135979000	1.961396000	0.215299000
C	-2.019905000	4.103506000	1.364312000
H	-2.452572000	5.078617000	1.612999000
C	-0.808347000	3.707586000	1.885405000
H	-0.256182000	4.348416000	2.576913000
C	-0.277753000	2.426611000	1.555019000
C	1.005925000	1.984230000	2.161762000
C	2.058365000	2.899264000	2.365375000
H	1.954367000	3.933587000	2.017720000
C	3.240043000	2.494208000	2.995445000
H	4.052607000	3.213171000	3.136587000
C	3.389054000	1.170192000	3.427583000
H	4.313381000	0.854479000	3.920227000
C	2.345162000	0.253448000	3.235527000
H	2.445623000	-0.777160000	3.590659000
C	1.160058000	0.657103000	2.612301000
H	0.325409000	-0.043999000	2.506406000
C	-2.707430000	-1.267990000	-1.285752000
C	-1.094850000	-1.629505000	-3.097456000
H	-0.062050000	-1.756935000	-2.724828000
H	-1.270491000	-0.562946000	-3.293856000
H	-1.199659000	-2.204914000	-4.033981000
C	-1.935526000	-3.549955000	-1.826825000
H	-2.281494000	-4.180603000	-2.664941000
H	-2.507227000	-3.803804000	-0.922922000
H	-0.863831000	-3.773725000	-1.639255000
C	-4.411711000	-1.207981000	0.507390000
H	-3.634871000	-0.650445000	1.049898000
H	-4.731630000	-2.073946000	1.115443000
H	-5.283454000	-0.543579000	0.354337000
C	-4.795227000	-2.603486000	-1.467247000
H	-4.432761000	-2.782729000	-2.487597000
H	-5.795067000	-2.134329000	-1.516273000
H	-4.892019000	-3.569064000	-0.938019000
C	2.221846000	-0.624221000	-1.826406000

E(RMN15L) = -3628.23659906
Zero-point correction = 0.771557 (Hartree/Particle)
Thermal correction to Energy = 0.817145
Thermal correction to Enthalpy = 0.818089
Thermal correction to Gibbs Free Energy = 0.695782

Cu(I) Cis conformer $C1_C$

N	0.000000000	1.843693000	1.159263000
C	0.125937000	2.045938000	2.472172000
N	1.277177000	1.650070000	3.082991000
C	2.470004000	1.429028000	2.276676000
H	2.440015000	0.450954000	1.753865000
H	3.343905000	1.450836000	2.946387000
H	2.564786000	2.227595000	1.525321000
N	-0.845200000	2.605908000	3.260643000
C	1.349643000	1.121644000	4.441420000
H	0.373031000	1.181646000	4.935822000
H	2.090991000	1.683230000	5.036103000

H	1.668308000	0.059824000	4.401658000
N	-1.248852000	1.033603000	-1.093111000
C	-0.530622000	3.532396000	4.345439000
H	-0.951930000	4.526298000	4.095742000
H	0.556527000	3.630718000	4.465104000
H	-0.975272000	3.195762000	5.299222000
C	-2.239660000	2.632441000	2.844711000
H	-2.871435000	2.412662000	3.723836000
H	-2.419883000	1.873898000	2.068821000
H	-2.524873000	3.626307000	2.446987000
C	-0.581458000	2.822227000	0.352410000
C	-0.508623000	4.197997000	0.592887000
H	-0.043305000	4.555831000	1.519587000
C	-0.978123000	5.135155000	-0.356803000
H	-0.890778000	6.202411000	-0.130676000
C	-1.517594000	4.724957000	-1.565478000
H	-1.862793000	5.447471000	-2.311725000
C	-1.613887000	3.337328000	-1.851110000
C	-1.167126000	2.383563000	-0.885464000
C	-2.116698000	2.825843000	-3.080252000
H	-2.464312000	3.528060000	-3.846193000
C	-2.149866000	1.464380000	-3.292809000
H	-2.533092000	1.042404000	-4.226147000
C	-1.715198000	0.581805000	-2.263952000
C	-1.772235000	-0.891969000	-2.446216000
C	-1.361865000	-1.497538000	-3.647269000
H	-0.992547000	-0.873045000	-4.470166000
C	-1.374686000	-2.891794000	-3.772026000
H	-1.022240000	-3.355943000	-4.698478000
C	-1.813404000	-3.693204000	-2.708998000
H	-1.813242000	-4.783096000	-2.807960000
C	-2.244568000	-3.093855000	-1.517001000
H	-2.590234000	-3.712322000	-0.680825000
C	-2.218346000	-1.703413000	-1.388504000
H	-2.552757000	-1.216226000	-0.470071000
Cu	0.000000000	0.000000000	0.224572000
N	0.000000000	-1.843693000	1.159263000
C	-0.125937000	-2.045938000	2.472172000
N	-1.277177000	-1.650070000	3.082991000
C	-2.470004000	-1.429028000	2.276676000
H	-2.440015000	-0.450954000	1.753865000
H	-3.343905000	-1.450836000	2.946387000
H	-2.564786000	-2.227595000	1.525321000
N	0.845200000	-2.605908000	3.260643000
C	-1.349643000	-1.121644000	4.441420000
H	-0.373031000	-1.181646000	4.935822000
H	-2.090991000	-1.683230000	5.036103000
H	-1.668308000	-0.059824000	4.401658000
N	1.248852000	-1.033603000	-1.093111000
C	0.530622000	-3.532396000	4.345439000
H	0.951930000	-4.526298000	4.095742000
H	-0.556527000	-3.630718000	4.465104000
H	0.975272000	-3.195762000	5.299222000
C	2.239660000	-2.632441000	2.844711000
H	2.871435000	-2.412662000	3.723836000
H	2.419883000	-1.873898000	2.068821000
H	2.524873000	-3.626307000	2.446987000
C	0.581458000	-2.822227000	0.352410000
C	0.508623000	-4.197997000	0.592887000
H	0.043305000	-4.555831000	1.519587000
C	0.978123000	-5.135155000	-0.356803000
H	0.890778000	-6.202411000	-0.130676000
C	1.517594000	-4.724957000	-1.565478000
H	1.862793000	-5.447471000	-2.311725000
C	1.613887000	-3.337328000	-1.851110000
C	1.167126000	-2.383563000	-0.885464000
C	2.116698000	-2.825843000	-3.080252000
H	2.464312000	-3.528060000	-3.846193000
C	2.149866000	-1.464380000	-3.292809000
H	2.533092000	-1.042404000	-4.226147000
C	1.715198000	-0.581805000	-2.263952000
C	1.772235000	0.891969000	-2.446216000
C	1.361865000	1.497538000	-3.647269000
H	0.992547000	0.873045000	-4.470166000
C	1.374686000	2.891794000	-3.772026000
H	1.022240000	3.355943000	-4.698478000
C	1.813404000	3.693204000	-2.708998000
H	1.813242000	4.783096000	-2.807960000
C	2.244568000	3.093855000	-1.517001000
H	2.590234000	3.712322000	-0.680825000
C	2.218346000	1.703413000	-1.388504000
H	2.552757000	1.216226000	-0.470071000

E(RMN15L) = -3628.24357793
Zero-point correction = 0.771556 (Hartree/Particle)
Thermal correction to Energy = 0.816704
Thermal correction to Enthalpy = 0.817648
Thermal correction to Gibbs Free Energy = 0.698109

Cu(II) Trans Conformer $C2_T$

Cu	-0.148793000	-0.008048000	-0.204208000
N	-2.021580000	0.384124000	-0.905071000
N	-0.401853000	1.827576000	0.611899000
C	2.918571000	-1.577471000	-2.624758000
H	3.397324000	-0.767360000	-3.185172000
N	-4.155346000	-0.687692000	-0.817902000
C	3.263170000	-2.921095000	-2.895453000
H	4.007263000	-3.129188000	-3.669171000
N	-2.382776000	-1.607329000	-2.016946000
C	2.689229000	-3.962738000	-2.185981000
H	2.980785000	-5.002114000	-2.361734000
N	1.466841000	0.013286000	-1.407524000
C	1.730111000	-3.680540000	-1.175376000
N	0.410086000	-1.982652000	0.020506000
C	1.332314000	-2.331635000	-0.939872000
N	3.556597000	1.118826000	-1.143536000
C	1.182327000	-4.673940000	-0.321075000
H	1.451894000	-5.723852000	-0.475921000
N	1.696679000	2.232182000	-2.017873000
C	0.363611000	-4.294575000	0.721235000
H	-0.027416000	-5.023931000	1.434314000
C	-0.014258000	-2.931305000	0.872917000
C	-0.794183000	-2.522215000	2.071217000
C	-0.318445000	-2.927958000	3.332541000
H	0.561596000	-3.577262000	3.392994000
C	-0.927959000	-2.457933000	4.500582000
H	-0.532237000	-2.756036000	5.475472000
C	-2.035913000	-1.605013000	4.420228000

H	-2.513261000	-1.237908000	5.332927000
C	-2.545300000	-1.237422000	3.167134000
H	-3.433031000	-0.601743000	3.107839000
C	-1.922924000	-1.690682000	1.999247000
H	-2.320494000	-1.429620000	1.017598000
C	-2.413601000	1.700640000	-0.678741000
C	2.259383000	1.104097000	-1.525549000
C	4.547329000	2.025432000	-1.724828000
H	5.432804000	1.426166000	-1.996551000
H	4.856872000	2.798544000	-0.998870000
H	4.145135000	2.501402000	-2.628096000
C	4.105935000	0.152830000	-0.193573000
H	4.644063000	-0.656806000	-0.717872000
H	3.303415000	-0.273708000	0.428112000
H	4.817067000	0.687714000	0.454971000
C	1.995446000	3.570678000	-1.513574000
H	2.612707000	3.505352000	-0.605797000
H	1.036034000	4.057163000	-1.257020000
H	2.511883000	4.190580000	-2.266651000
C	0.565636000	2.148138000	-2.941100000
H	0.631397000	3.001484000	-3.635252000
H	-0.404130000	2.200591000	-2.413351000
H	0.620214000	1.212172000	-3.512929000
C	-3.529486000	2.343115000	-1.223097000
H	-4.232124000	1.776728000	-1.841526000
C	-3.743103000	3.724697000	-1.014347000
H	-4.621176000	4.193094000	-1.467434000
C	-2.870250000	4.483298000	-0.251196000
H	-3.049414000	5.546434000	-0.067235000
C	-1.723875000	3.869020000	0.319448000
C	-1.492089000	2.479700000	0.096817000
C	-0.787002000	4.555693000	1.138531000
H	-0.938363000	5.620367000	1.344468000
C	0.278960000	3.873206000	1.686395000
H	0.979999000	4.368305000	2.361819000
C	0.457226000	2.489883000	1.403527000
C	1.559884000	1.727274000	2.038151000
C	2.823369000	2.317731000	2.243449000
H	3.020372000	3.327665000	1.866921000
C	3.827079000	1.617908000	2.919368000
H	4.806191000	2.082641000	3.065842000
C	3.585311000	0.321868000	3.395681000
H	4.371994000	-0.221104000	3.927053000
C	2.329549000	-0.270981000	3.203962000
H	2.124616000	-1.270383000	3.599937000
C	1.319714000	0.428100000	2.535673000
H	0.315042000	-0.003422000	2.457556000
C	-2.876309000	-0.597977000	-1.253794000
C	-1.400111000	-1.360292000	-3.069408000
H	-0.448877000	-1.873817000	-2.848395000
H	-1.222073000	-0.282020000	-3.168526000
H	-1.791113000	-1.758312000	-4.022325000
C	-2.704977000	-3.011298000	-1.773528000
H	-3.338474000	-3.443979000	-2.567991000
H	-3.209306000	-3.120248000	-0.801362000
H	-1.751274000	-3.573000000	-1.743213000
C	-4.627746000	-0.070578000	0.419334000
H	-3.793263000	0.371995000	0.978074000
H	-5.109853000	-0.850750000	1.035151000
H	-5.369406000	0.717104000	0.198963000
C	-5.192077000	-1.402231000	-1.566749000
H	-4.851741000	-1.595007000	-2.592061000
H	-6.087346000	-0.759259000	-1.597444000
H	-5.461585000	-2.354355000	-1.077585000
C	1.954080000	-1.264623000	-1.663996000

E(UMN15L) = -3628.05890574
Zero-point correction = 0.774196 (Hartree/Particle)
Thermal correction to Energy = 0.819196
Thermal correction to Enthalpy = 0.820140
Thermal correction to Gibbs Free Energy = 0.699272

Cu(II) Cis Conformer $C2_C$

N	0.000000000	1.736993000	1.175315000
C	0.160944000	1.936043000	2.505940000
N	1.284764000	1.449220000	3.078702000
C	2.486234000	1.249480000	2.266063000
H	2.466128000	0.282853000	1.728056000
H	3.355048000	1.258598000	2.940669000
H	2.582846000	2.067948000	1.537213000
N	-0.750286000	2.589839000	3.269763000
C	1.405016000	1.041813000	4.477750000
H	0.434712000	1.097483000	4.982978000
H	2.130441000	1.678550000	5.011892000
H	1.772798000	-0.001582000	4.508689000
N	-1.138105000	1.056852000	-1.134483000
C	-0.372755000	3.454628000	4.390312000
H	-0.803522000	4.454780000	4.202326000
H	0.718913000	3.546038000	4.454895000
H	-0.774129000	3.074971000	5.345772000
C	-2.153778000	2.706525000	2.882077000
H	-2.776614000	2.489626000	3.767035000
H	-2.394915000	1.993747000	2.082314000
H	-2.379303000	3.731164000	2.533992000
C	-0.482017000	2.778901000	0.373780000
C	-0.348625000	4.144266000	0.643765000
H	0.088516000	4.473281000	1.592931000
C	-0.726332000	5.113102000	-0.315397000
H	-0.588805000	6.170204000	-0.071281000
C	-1.257445000	4.750370000	-1.543430000
H	-1.563686000	5.502049000	-2.276706000
C	-1.416617000	3.374262000	-1.854352000
C	-1.025355000	2.396804000	-0.894100000
C	-1.946249000	2.893423000	-3.082607000
H	-2.260276000	3.614733000	-3.844676000
C	-2.066556000	1.535387000	-3.300119000
H	-2.496850000	1.140465000	-4.223898000
C	-1.646309000	0.621380000	-2.296930000
C	-1.780204000	-0.844372000	-2.473938000
C	-1.419859000	-1.475666000	-3.678033000
H	-1.025913000	-0.877406000	-4.508782000
C	-1.514990000	-2.866600000	-3.791405000
H	-1.202555000	-3.356452000	-4.718444000
C	-1.987284000	-3.634870000	-2.717095000
H	-2.053456000	-4.722835000	-2.810964000
C	-2.375681000	-3.007406000	-1.525427000
H	-2.758771000	-3.599249000	-0.687107000
C	-2.269417000	-1.619740000	-1.406703000

H	-2.592986000	-1.106466000	-0.498096000
Cu	0.000000000	0.000000000	0.156221000
N	0.000000000	-1.736993000	1.175315000
C	-0.160944000	-1.936043000	2.505940000
N	-1.284764000	-1.449220000	3.078702000
C	-2.486234000	-1.249480000	2.266063000
H	-2.466128000	-0.282853000	1.728056000
H	-3.355048000	-1.258598000	2.940669000
H	-2.582846000	-2.067948000	1.537213000
N	0.750286000	-2.589839000	3.269763000
C	-1.405016000	-1.041813000	4.477750000
H	-0.434712000	-1.097483000	4.982978000
H	-2.130441000	-1.678550000	5.011892000
H	-1.772798000	0.001582000	4.508689000
N	1.138105000	-1.056852000	-1.134483000
C	0.372755000	-3.454628000	4.390312000
H	0.803522000	-4.454780000	4.202326000
H	-0.718913000	-3.546038000	4.454895000
H	0.774129000	-3.074971000	5.345772000
C	2.153778000	-2.706525000	2.882077000
H	2.776614000	-2.489626000	3.767035000
H	2.394915000	-1.993747000	2.082314000
H	2.379303000	-3.731164000	2.533992000
C	0.482017000	-2.778901000	0.373780000
C	0.348625000	-4.144266000	0.643765000
H	-0.088516000	-4.473281000	1.592931000
C	0.726332000	-5.113102000	-0.315397000
H	0.588805000	-6.170204000	-0.071281000
C	1.257445000	-4.750370000	-1.543430000
H	1.563686000	-5.502049000	-2.276706000
C	1.416617000	-3.374262000	-1.854352000
C	1.025355000	-2.396804000	-0.894100000
C	1.946249000	-2.893423000	-3.082607000
H	2.260276000	-3.614733000	-3.844676000
C	2.066556000	-1.535387000	-3.300119000
H	2.496850000	-1.140465000	-4.223898000
C	1.646309000	-0.621380000	-2.296930000
C	1.780204000	0.844372000	-2.473938000
C	1.419859000	1.475666000	-3.678033000
H	1.025913000	0.877406000	-4.508782000
C	1.514990000	2.866600000	-3.791405000
H	1.202555000	3.356452000	-4.718444000
C	1.987284000	3.634870000	-2.717095000
H	2.053456000	4.722835000	-2.810964000
C	2.375681000	3.007406000	-1.525427000
H	2.758771000	3.599249000	-0.687107000
C	2.269417000	1.619740000	-1.406703000
H	2.592986000	1.106466000	-0.498096000

E(UMN15L) = -3628.07256396
Zero-point correction = 0.774795 (Hartree/Particle)
Thermal correction to Energy = 0.819274
Thermal correction to Enthalpy = 0.820218
Thermal correction to Gibbs Free Energy = 0.702529

11.4 Crest calculations: Best Conformers

Crest_best Starting from $C1_T$

93
-135.25382623

Cu	-0.0183872851	-0.4049273019	0.0482966191
N	1.9175964667	-1.1247509171	0.0557809307
N	0.8043503716	1.0528735809	1.2344592003
C	-4.1514509543	-0.3962785562	-0.3429612923
H	-4.5704640068	-1.2923543891	0.0912674150
N	1.8408052799	-3.2315984930	-0.8575636479
C	-5.0053308486	0.6395184664	-0.7238284595
H	-6.0710755345	0.5103239913	-0.5989349271
N	3.1541140444	-2.8844166885	1.0353743068
C	-4.5154341908	1.8102061960	-1.2417526367
H	-5.1772140226	2.6131060576	-1.5322017128
N	-1.8959288808	-1.2307429347	-0.0328487484
C	-3.1275180275	1.9749459407	-1.3953833336
N	-0.9194756485	1.0049450728	-1.2035657253
C	-2.2521902846	0.9215772559	-1.0309558653
N	-1.6753027189	-3.2920455531	0.9517243913
C	-2.5343141416	3.1504886085	-1.9044497628
H	-3.1670442262	3.9808890136	-2.1872519512
N	-2.7835357583	-3.1431614314	-1.0895518989
C	-1.1764787776	3.2223711600	-2.0377684496
H	-0.7020829928	4.1046186995	-2.4397395922
C	-0.3832903335	2.1085969209	-1.6850664387
C	1.0680312798	2.1385535719	-1.9116444629
C	1.7044655105	1.0190644337	-2.4389580932
H	1.1166934351	0.1424068675	-2.6547158718
C	3.0599752362	1.0456585615	-2.7054857063
H	3.5456955802	0.1790792053	-3.1275229769
C	3.7984706655	2.1864921038	-2.4419778175
H	4.8574280972	2.2123756260	-2.6516051151
C	3.1747840931	3.3007014653	-1.9063037825
H	3.7493589464	4.1904228852	-1.6928993298
C	1.8171310321	3.2817700522	-1.6465740692
H	1.3412826353	4.1504504194	-1.2147719356
C	2.7314658412	-0.0930655128	0.4493179034
C	-2.1432439329	-2.5277750618	-0.0539450469
C	-1.2259109850	-4.6574661659	0.7797900667
H	-1.3176585184	-4.9585345921	-0.2578033642
H	-1.8057628422	-5.3388211356	1.4054863549
H	-0.1797320471	-4.7207932593	1.0782676265
C	-1.1725575066	-2.6235967730	2.1288451496
H	-0.2337293914	-2.0981536304	1.9064145632
H	-1.0145088945	-3.3595263856	2.9132573883
H	-1.9015887387	-1.8882652728	2.4614564980
C	-3.6937005636	-4.2550068778	-0.8962816054
H	-3.7646526079	-4.5105181233	0.1561067377
H	-3.3720667233	-5.1294889828	-1.4662009455
H	-4.6884251780	-3.9687828634	-1.2493384598
C	-2.9064603789	-2.4966591346	-2.3754165886
H	-2.0823279727	-1.8042058365	-2.5225083288
H	-3.8464857980	-1.9472001057	-2.4772769589
H	-2.8686024400	-3.2646269727	-3.1472370535
C	4.0997816959	-0.0757283179	0.2233666868
H	4.5743451970	-0.9292326411	-0.2373510757

C	4.8760319951	1.0389586226	0.5371761824
H	5.9387590412	1.0079154284	0.3440776111
C	4.3113613858	2.1700015788	1.0665604786
H	4.9105644994	3.0376566844	1.2972578308
C	2.9247248655	2.2126476144	1.2919668161
C	2.1313229565	1.0748822939	1.0022173387
C	2.2540258917	3.3508972057	1.7912285161
H	2.8246834488	4.2411491566	2.0158885030
C	0.9011636680	3.3146230960	1.9790845009
H	0.3646486482	4.1671986310	2.3690410764
C	0.1958784715	2.1255441781	1.6981204513
C	-1.2459475102	2.0365300029	1.9703660145
C	-2.1203649489	3.0465026861	1.5829055799
H	-1.7464715054	3.9028439415	1.0394927335
C	-3.4698755590	2.9447804301	1.8684506185
H	-4.1447203507	3.7284314353	1.5570295693
C	-3.9567479253	1.8459649057	2.5564512907
H	-5.0095794243	1.7780522903	2.7885159020
C	-3.0897724747	0.8416097944	2.9528890134
H	-3.4667446626	-0.0065603930	3.5050926784
C	-1.7428074959	0.9322325809	2.6559557255
H	-1.0520912428	0.1699565418	2.9786800465
C	2.3350837496	-2.3788094569	0.0565788934
C	3.1985134953	-2.2551372731	2.3368177703
H	4.0558682551	-1.5851369334	2.4470230870
H	3.2750980093	-3.0401895165	3.0903157583
H	2.2898741886	-1.6865886339	2.5069288580
C	4.3343887329	-3.6723446069	0.7378508937
H	4.3958996204	-3.8936633251	-0.3222985067
H	4.3308185491	-4.6033549283	1.3069072493
H	5.2283086611	-3.1082707160	1.0199216854
C	1.1078158613	-2.7075281340	-1.9883249053
H	1.7778528399	-2.2027605658	-2.6843638026
H	0.3631856268	-1.9845704342	-1.6363909824
H	0.6128136866	-3.5234180450	-2.5038984255
C	1.9665840178	-4.6699802404	-0.7719212531
H	2.7556884688	-5.0445251625	-1.4287286574
H	1.0282725809	-5.1260337488	-1.0837220408
H	2.1805226365	-4.9687487463	0.2496560058
C	-2.7763154933	-0.2862995768	-0.4824578815

Crest_best Starting from $C1_C$

93

-135.25695536

N	-0.1479836929	-2.2066074577	-0.2784391192
C	-1.1917244203	-2.9894035709	-0.4875307928
N	-1.9735741704	-2.7282622394	-1.5537366673
C	-1.4646674694	-1.8330592850	-2.5672110603
H	-2.1302430499	-1.8543641536	-3.4262663213
H	-0.4735577133	-2.1598798567	-2.8793993983
H	-1.3831350352	-0.8103993025	-2.1792342490
N	-1.5552101096	-4.0028752606	0.3523458064
C	-3.3924082106	-3.0035489162	-1.6211869799
H	-3.7442132218	-3.4138699997	-0.6821834110
H	-3.6137074855	-3.7066162844	-2.4277285015
H	-3.9212317132	-2.0708689739	-1.8213647179
N	1.5137540573	-0.4967578799	1.0443799306
C	-2.0967580001	-5.2579394285	-0.1321168642
H	-1.4292815742	-6.0726289147	0.1618101636
H	-2.1692058837	-5.2522299765	-1.2145115539
H	-3.0790182810	-5.4571946623	0.3005549945
C	-1.0403945748	-4.0761667652	1.7004344784
H	-1.8464095906	-4.4018970272	2.3615174802
H	-0.6849249247	-3.1002631608	2.0203494935
H	-0.2152754661	-4.7914469065	1.7849604885
C	1.0558410162	-2.6696482573	0.1776751521
C	1.5148626192	-3.9552373908	-0.0794089208
H	0.8767401664	-4.6477918406	-0.6084313510
C	2.7960555220	-4.3613835500	0.2887784507
H	3.1093476051	-5.3722796862	0.0699743886
C	3.6601473040	-3.4947358909	0.9066546094
H	4.6570922910	-3.8025325585	1.1845692637
C	3.2538596921	-2.1745425732	1.1654309093
C	1.9451413409	-1.7533544735	0.8150987342
C	4.0987093800	-1.2134661442	1.7600056235
H	5.0997573337	-1.4989311473	2.0514268765
C	3.6469160746	0.0605765624	1.9488345693
H	4.2745929708	0.8079298961	2.4083801000
C	2.3305413289	0.3992490421	1.5670014380
C	1.8464266937	1.7741977107	1.7504121527
C	2.6936282968	2.8586818743	1.5292508429
H	3.7130332551	2.6903001200	1.2142938104
C	2.2297733388	4.1519276668	1.6811176346
H	2.8934469164	4.9845690212	1.4969721696
C	0.9195973178	4.3824626222	2.0681669146
H	0.5610577068	5.3940754307	2.1870733202
C	0.0743279920	3.3107551272	2.3017078836
H	-0.9463498541	3.4887078076	2.6048123692
C	0.5321690657	2.0169799894	2.1403759625
H	-0.1198573812	1.1792130211	2.3234000156
Cu	-0.2131034270	-0.1384575178	0.0092980494
N	-2.0510667881	0.8162989714	0.2835951819
C	-3.2237231684	0.2349235614	0.4662906229
N	-3.3628399811	-0.5932794107	1.5199336764
C	-2.3461413960	-0.5598033993	2.5465673645
H	-2.2184464025	0.4606971720	2.9039559102
H	-1.3842601720	-0.9080016018	2.1534497344
H	-2.6582038033	-1.1876723177	3.3757527953
N	-4.2763582040	0.3764328641	-0.3943534951
C	-4.2529124824	-1.7325103927	1.5660452101
H	-4.8263617292	-1.8087283734	0.6507873210
H	-4.9369605956	-1.6490674341	2.4129287346
H	-3.6594055511	-2.6391638446	1.6906680799
N	0.2271645272	1.5698941352	-1.0244184879
C	-5.6473588139	0.4812855682	0.0698051793
H	-6.0478837039	1.4581129606	-0.2147595502
H	-5.6965718244	0.3960601766	1.1504998012
H	-6.2757498603	-0.2851447488	-0.3881561551
C	-4.0775014171	0.9071335094	-1.7237384968
H	-4.7956359002	0.4303011294	-2.3915234369
H	-3.0691415806	0.6892667183	-2.0651673681
H	-4.2320754286	1.9904883748	-1.7675088234
C	-1.9241698800	2.1079874056	-0.1478572454
C	-2.8685764541	3.0867620690	0.1357148675
H	-3.7647319902	2.8137776750	0.6738755411
C	-2.6717340199	4.4192575978	-0.2208745027

H	-3.4360173291	5.1451452148	0.0176750044
C	-1.5237352836	4.8147604526	-0.8572180781
H	-1.3649251643	5.8463701786	-1.1334452408
C	-0.5227751678	3.8689504129	-1.1373887513
C	-0.7137692262	2.5067624838	-0.7893151020
C	0.6998469242	4.2069213925	-1.7548917826
H	0.8749000095	5.2308613037	-2.0536284445
C	1.6448907825	3.2432527010	-1.9562580823
H	2.5819531053	3.4794370395	-2.4354341479
C	1.3845356422	1.9132623399	-1.5593160045
C	2.4169566703	0.8844834029	-1.7451971262
C	3.7644443514	1.1914481553	-1.5617734177
H	4.0550368179	2.1889518391	-1.2664991083
C	4.7332880225	0.2196825448	-1.7280157493
H	5.7737861992	0.4685400350	-1.5758263042
C	4.3752431199	-1.0691498491	-2.0894156909
H	5.1357239223	-1.8243087920	-2.2219269887
C	3.0398335201	-1.3817622371	-2.2797853700
H	2.7579405971	-2.3854413880	-2.5602381450
C	2.0687837505	-0.4140409444	-2.1060088190
H	1.0288236106	-0.6497308203	-2.2551185807